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**Mean Amplitudes of Vibration
In Molecular Structure Studies**

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1. REVIEW OF THE STUDY ON MEAN AMPLITUDES OF VIBRATION *)

1.1. Introduction

Definition of the mean amplitude of vibration. Let the instantaneous intramolecular distance between an arbitrary pair of atoms be denoted by R and the equilibrium distance by R_e. The root-mean-square deviation

$$u = \left[\overline{(R - R_e)^2} \right]^{\frac{1}{2}} \qquad (1.1)$$

will be called the m e a n   a m p l i t u d e   o f v i b r a t i o n **) and its square (u^2) the m e a n – s q u a r e   a m p l i t u d e   o f   v i b - r a t i o n . Occasionally these terms are used in a

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*) See also references (42), (36).

**) Some other designations which have been attached to the quantity of u are "average amplitude of vibrations" or "average displacement from equilibrium" [Karle et al., see (73), (74), Bastiansen et al.(5)], "mean amplitude of thermal vibrations" [Morino et al. (93), (97), (98), (94)], "rms amplitude of vibration" (95), (66), and "standard deviation of the interatomic distance" [Bastiansen et al.(19), (25), (27)]. Symbols similar to $\langle 1^2 \rangle_{Av}^{\frac{1}{2}}$, $\langle \Delta r^2 \rangle_{Av}^{\frac{1}{2}}$, etc. for the mean amplitude of vibration are frequently used in the literature.

1.1.

more general sense where the meaning of $R-R_e$ in equation (1) is not restricted to an interatomic distance deviation, but used to denote an arbitrary displacement coordinate (e.g. an angle deformation).

The concept of mean-square amplitudes has been extended by Morino et al. (94) in the following way. Since a product of two vectors $(R-R_e)$ is a tensor with six different cartesian components, it will be appropriate to introduce $\overline{(\Delta z)^2}$, called the m e a n - s q u a r e   p a r a l l e l   a m p l i t u d e, $\overline{(\Delta x)^2}$ and $\overline{(\Delta y)^2}$ as the m e a n - s q u a r e p e r p e n d i c u l a r   a m p l i t u d e s, and the m e a n   c r o s s   p r o d u c t s $\overline{\Delta x \Delta y}$, $\overline{\Delta y \Delta z}$ and $\overline{\Delta z \Delta x}$. The quantity defined by equation (1) coincides to the first order of approximation with the square-root of the parallel component, viz. $\left[\overline{(\Delta z)^2}\right]^{\frac{1}{2}}$, where the z-axis is chosen in the direction of the line connecting the atom pair at the equilibrium position.

Utility of mean amplitudes of vibration. The importance of mean amplitudes of vibration in molecular structure studies will be understood from the following statements. As is well known, the rigid model of a polyatomic molecule of given symmetry in its equilibrium position, is defined by a certain number of parameters, i.e. interatomic distances and occasionally some inter-bond angles. To define the actual non-rigid molecular model, an additional set of parameters are required. For this purpose the mean amplitudes of vibration are very suitable.

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1.1.

Principles for determining values of u. Mean
amplitudes of vibration are determined by the two
largely different methods of electron-diffraction and
molecular spectroscopy. There is, however, no theoreti-
cal foundation for the practice of referring to the
mean amplitudes of vibration from electron-diffraction
as "observed" in contrary to the spectroscopical ones
as "calculated". The mean amplitudes of vibration are
not directly observed by either of the methods, but
are obtained from complicated computations from the
measured and interpreted experimental data.

In the case of the electron-diffraction method,
the determination of mean amplitudes of vibration was
made possible by the progress of modern experimental
techniques with the sector method [see, e.g. references
(12a),(17)]. "The experimental determination of the values
of u is based upon the study of the natural damping of
the various sine-terms making up the electron diffrac-
tion intensity curve. By the visual method these natural
damping factors could scarcely be obtained. The sector
method, however, makes this kind of study possible.
To secure reliable values all effects causing extra
damping must be avoided, and the geometry of the
electron diffraction apparatus must permit the study
of the largest obtainable diffraction angles." (19)

The computations of mean amplitudes of vibration
from spectroscopic data are based on the vibrational
frequencies as obtained from the assignment of observed
frequencies in the infrared and Raman. This field will
be treated extensively in the following chapters of the
present thesis.

1.2.

1.2. Survey of the work on mean amplitudes of vibration
from electron-diffraction

The estimation of mean amplitudes of vibration from electron-diffraction data was started by I.Karle and J. Karle [73], [77], [74] with their investigations of carbon dioxide and carbon tetrachloride molecules. The work was based on the fundamental paper of Debye [46] concerning the influence of intramolecular motion on electron-diffraction diagrams.

Some features of the theory will be considered briefly in the following. For detailed studies, see Viervoll [128] and others of the cited papers. The intensity from molecular scattering is given by

$$I_m = \sum_{i \neq j} (Z_i - F_i)(Z_j - F_j) \exp[-a_{ij} s^2] \frac{\sin sR_e}{sR_e}$$

$$= \int_0^\infty \sigma(R) \frac{\sin sR}{sR} dR . \qquad (1.2)$$

By a Fourier transform, the radial distribution function is obtained as

$$\frac{\sigma(R)}{R} = \frac{2}{\pi} \int_0^\infty sI_m \sin sR \, ds \approx$$

$$\sum_{i \neq j} \frac{n_{ij} Z_i Z_j}{R_e} \frac{1}{u(2\pi)^{\frac{1}{2}}} \exp\left[- \frac{(R-R_e)^2}{4a_{ij}}\right] , \qquad (1.3)$$

where mainly the same notation is used as that of the paper of Viervoll [129]. The quantities of a_{ij} are related to the mean amplitudes of vibration (u) according

1.2.

to $a_{ij} = \frac{1}{2}u^2$. Hence the value of u for a given inter-
atomic distance may be obtained from the respective
Gaussian curve of the radial distribution. If the
half-width of a given Gaussian-shaped peak is denoted
by B, one has

$$u = (8 \ln 2)^{-\frac{1}{2}} B . \tag{1.4}$$

In practice it will be advantageous to introduce an
artificial damping factor e^{-ks^2} multiplying the
intensity in equation (2). The effect on the radial
distribution curve is a broadening of each of the
Gaussian peaks, without displacing their maximum
positions. In accordance, the following expression is
found for the mean amplitude of vibration.

$$u = \left[(B^2/8 \ln 2) - 2k\right]^{\frac{1}{2}} . \tag{1.5}$$

The theory has been revised and extended by Morino
et al.([94]). Another refinement was developed by Bartell
et al.([44]), who included the effect caused by the
failure of the Born approximation ([112]),([54]), and re-
ported their corrected values of mean amplitudes of
vibration for carbon tetrachloride ([15]).

The effect of anharmonicity is of great impor-
tance in electron-diffraction studies of mean amplitudes
of vibration, and has actually been observed ([3]),([18]).
Concerning the theory, reference is made to a treatment
by Bartell ([11]).

A general discussion of the sources of errors in
the determination of mean amplitudes of vibration by
electron-diffraction has been given by Kuchitsu ([87]).

1.2.

He pointed out that the finite sample size of the
diffracting center is another important factor intro-
ducing an error to the mean amplitudes of vibration.

Internal rotation represents a kind of intra-
molecular motion that has been subjected to several
extensive investigations. This field, however, shall
not be dealt with in the present work.

References to electron-diffraction works in-
cluding mean amplitudes of vibration of individual
molecules are summarized in Table I.

1.3. Survey of the work on mean amplitudes of vibration
from spectroscopic data

Nearly all of the reported calculations of mean
amplitudes of vibration from spectroscopic data are
based on the assumption of small harmonic vibrations.
The earliest computations are reported by Debye (46),
who gives a formula for diatomic molecules, and calcu-
lations for carbon dioxide. Morino (93) pointed out
that Karle's electron-diffraction values for carbon
dioxide (73) were in excellent agreement with the
spectroscopical ones, if a correction was made to
Debye's calculation. An extensive treatment and
development of the general method of computing mean
amplitudes of vibration for polyatomic molecules is
due to Morino et al. (97), (98), (94) [see also Decius (48)],
and based on the theory of Bloch (22) and James (70).
One of these papers (94) is concerned with the extended
theory including the mean-square perpendicular ampli-
tudes and mean cross products.

1.3.

The mean-square amplitude of vibration for a diatomic molecule, treated as a harmonic oscillator, is given by $u^2 = u_o^2 \coth(h\beta\nu/2)$, $\beta = 1/kT$ (k = Boltzmann's constant, T = absolute temperature), and

$$u_o^2 = h/8\pi^2\nu\mu \approx h/4\pi(k\mu)^{\frac{1}{2}} = h\nu/2k \ . \qquad (1.6)$$

Here ν is the vibrational frequency, k the force constant, and u the reduced mass. For the mean-square amplitude of vibration for a given interatomic distance of a polyatomic molecule, one has

$$u^2 = \overline{(\Delta R_1)^2} = \sum_k K_{ik}^2(h/8\pi^2\nu_k)\coth(h\beta\nu_k/2), \qquad (1.7)$$

where   represents the normal vibrational frequencies, and K_{ik} are the coefficients of the transformation to vibrational normal coordinates, viz.

$$\Delta R_1 = \sum K_{ik} Q_k \ . \qquad (1.8)$$

The quantities of K_{ik} may be calculated if all the force constants of the molecule are known. To determine the force constants from the normal frequencies, a normal-coordinate analysis is to be performed [see, e.g. [132], [133], [91], [136]]. It should be pointed out that the number of normal frequencies usually is insufficient for the determination of the complete harmonic force field. Consequently additional assumptions must be made. The method of calculating mean amplitudes of vibration according to equation (7) is treated extensively in chapter 2 of the present thesis.

1.3.

A special contribution to the theory of mean amplitudes of vibration has been developed by Cyvin (32),(39), who produced a new secular equation, relating the mean-square amplitudes of vibration to the normal frequencies. The relations do not involve the force constants, but other unknown quantities, referred to as the "interaction mean-square amplitudes". The new method is physically equivalent to that of Morino et al. described above, but differs only in the mathematical techniques. It may have certain advantages for solving some vibrational problems, and depending on the special conditions it supplements Morino's method.

Morino et al.(98) also propose approximate methods of calculating mean amplitudes of vibration. Furthermore, approximate characteristic values of mean amplitudes of vibration for a number of bonded and non-bonded atom pairs are tabulated. K. Kimura (80),(79) and M. Kimura (79) report approximate calculations of mean amplitudes of vibration for bonded distances, and a treatment of the effect of isotope substitution, including characteristic values for some bonded atom pairs. For the C-H bond in particular, the characteristic mean amplitudes of vibration have been studied by Cyvin (26), who also has developed a special approximate method of calculating mean amplitudes of vibration (37). This method is treated in chapter 5.

The anharmonicity effect has been treated extensively by Reitan (108),(109),(110), and numerical computations for some diatomic and symmetrical triatomic molecules are reported.

The subject of internal rotation has also been studied extensively by spectroscopical methods, but

1.3.

falls outside the scope of the present work.

References to mean amplitudes of vibration of individual molecules as calculated from spectroscopic data are collected in Table II.

1.4. Correlation between mean amplitudes of vibration from electron-diffraction and spectroscopic data

It may be stated that at present the mean amplitudes of vibration in general may be estimated with greater accuracy from spectroscopic data than from electron-diffraction, in cases when reliable force constants of the molecule have been determined from molecular spectra. The majority of cases studied show a satisfactory agreement between the values obtained from the two different methods, provided that proper limits of error are taken into consideration. In Table III a collection of examples is given.

1.5. Use of mean amplitudes of vibration for determining force constants

A precise knowledge of some mean amplitudes of vibration of a molecule may serve as additional information to the normal frequencies, for determining the force constants of the molecule. It may be stated that the comparatively great accuracy for the mean amplitudes of vibration which is claimed for this purpose, is difficult to reach by present electron-diffraction experiments. The first successfull investigations in

1.5.

this field are due to Morino et al.[99], who determined
the complete harmonic force field of germanium tetra-
chloride and carbon tetrachloride by means of mean
amplitudes of vibration from electron-diffraction,
combined with the vibrational frequencies from spectro-
scopic data. For the calculation of force constants
from known u-values, Cyvin's secular equation method
[32],[39] has proved to be useful. Some aspects of the
use of mean amplitudes of vibration in force constant
determinations are treated in chapter 6.

**Table I. References to computed mean amplitudes of vibration
from electron-diffraction.**

Molecule	Reference
O_2	Karle [72].
Br_2	Karle [72].
I_2	Karle [72], Almenningen, Bastiansen and Trætteberg [7].
CO_2	Karle and Karle [73].
PH_3	Bartell and Hirst [16].
S_2Cl_2	Hirota [66].
S_2Br_2	Hirota [66].
CCl_4	Karle and Karle [73], Bartell, Brockway and Schwendeman [15], Morino, Nakamura and Iijima [99].
$GeCl_4$	Morino, Nakamura and Iijima [99].
$TiCl_4$	Kimura, Kimura, Aoki and Shibata [61].

1.(Tables)

Table I (Continued).

$ZrCl_4$	Kimura, Kimura, Aoki and Shibata [84].
CH_3Cl	Bartell and Brockway [13].
CF_3Cl	Bartell and Brockway [13].
$HCOOH$	Karle and Karle [76].
CH_2CH_2	Bartell and Bonham [12].
CF_2CF_2	Karle and Karle [74]
CCl_2CCl_2	Karle and Karle [75].
CH_2CF_2	Karle and Karle [74]
CH_3OH	Kimura, Kimura and Shibata [85], Kimura and Kubo [84].
CH_2CCH_2 (Allene)	Almenningen, Bastiansen and Trætteberg [6].
CF_3CF_3	Swick and Karle [119].
CCl_3CCl_3	Swick, Karle and Karle [120], Morino and Hirota [95].
$SiCl_3SiCl_3$	Swick and Karle [119], Morino and Hirota [95].
CH_3SiH_3	Bond and Brockway [23].
CCl_3SiCl_3	Morino and Hirota [95].
CH_2ClCH_2Cl	Ainsworth and Karle [1].
CF_2ClCF_2Cl	Iwasaki [67].
$CFCl_2CFCl_2$	Iwasaki, Nagase and Kojima [69].
$CF_2ClCFCl_2$	Iwasaki [68].
C_3H_6 (Cyclopropane)	Bastiansen and Cyvin [18].
$(CH_3)_2O$ (Dimethyl ether)	Kimura and Kubo [81].

1.(Tables)

Table I (Continued).

$C_4H_4Cl_2$(1.4.—di-chlorobutyne)   Kuchitsu [16].

C_3H_7Cl(n-propyl chloride)   Morino and Kuchitsu [36].

$(CH_3)_2SiH_2$ Bond and Brockway [13].

C_6H_6 (Dimethyl-diacetylene)   Almenningen, Bastiansen and Munthe-Kaas [5].

C_6H_6 (Benzene)   Karle [71], Bastiansen and Cyvin [19], Almenningen, Bastiansen and Fernholt [4].

S_2F_{10} Harvey and Bauer [59].

C_4H_{10}(n-butane)   Kuchitsu [67], Bonham and Bartell [24].

$(CH_3)_3SiH$ Bond and Brockway [13].

C_7H_6O (Tropone)   Kimura, Suzuki, Kimura and Kubo [83], [82].

C_7H_8 (Toluene)   Keidel and Bauer [76].

C_6SiH_8 (Phenyl-silane)   Keidel and Bauer [76].

C_8H_8 (Cyclooctatetraene)   Karle [71], Bastiansen, Hedberg and Hedberg [20].

$C_{12}H_{10}$(Biphenyl)   Almenningen and Bastiansen [2].

Table II. References to computed mean amplitudes of vibration from spectroscopic data.

Molecule	Reference
H_2	Reitan [108], [110].
O_2	Karle [72].

1.(Tables)

Table II (Continued).

Br_2	Karle [72], Reitan [110].
I_2	Karle [72].
CO_2	Debye [46], Karle and Karle [73], Morino [93], Reitan [109], Cyvin [41].
CS_2	Cyvin [41].
CSe_2	Cyvin [41].
COS	Cyvin [41].
$COSe$	Cyvin [41].
$CSSe$	Cyvin [41].
$CSTe$	Cyvin [41].
H_2O	Reitan [109].
NO_2	Cyvin [30].
O_3	Kimura [79].
P_4	Bakken [10], Cyvin and Bakken [44], Cyvin [29].
C_2H_2	Bakken [10].
C_2D_2	Bakken [10].
C_2HD	Bakken [10].
BF_3	Bakken [10], Cyvin [28], [31].
BCl_3	Bakken [10], Cyvin [28], [31].
BBr_3	Bakken [10], Cyvin [28], [31].
BI_3	Cyvin [28], [34].
NH_3	Cyvin and Bakken [44].
ND_3	Cyvin and Bakken [44].

1.(Tables)

Table II (Continued).

NF_3	Bakken [10].
PH_3	Bakken [10], Cyvin and Bakken [14], Bartell and Hirst [16].
PF_3	Bakken [10].
PCl_3	Bakken [10].
AsH_3	Bakken [10], Cyvin and Bakken [14].
SbH_3	Bakken [10], Cyvin and Bakken [14].
CH_2O	Bakken [10], Cyvin and Bakken [14].
CD_2O	Bakken [10].
S_2Cl_2	Hirota [66].
S_2Br_2	Hirota [66].
CCl_4	Karle and Karle [73], Morino, Kuchitsu, Takahashi and Maeda [98], Morino, Nakamura and Iijima [99].
$SiCl_4$	Kimura, Kimura, Aoki and Shibata [84].
$GeCl_4$	Kimura, Kimura, Aoki and Shibata [84], Morino, Nakamura and Iijima [99].
$SnCl_4$	Kimura, Kimura, Aoki and Shibata [84].
$TiCl_4$	Kimura, Kimura, Aoki and Shibata [84].
$ZrCl_4$	Kimura, Kimura, Aoki and Shibata [84].
CH_3Cl	Cyvin [43].
CD_3Cl	Cyvin [43].
CH_3Br	Cyvin [43].
CD_3Br	Cyvin [43].

1.(Tables)

<div align="center">Table II (Continued).</div>

CH_3I	Cyvin [43].
CD_3I	Cyvin [43].
CH_2CH_2	Bartell and Bonham [12].
CF_2CF_2	Morino, Kuchitsu and Shimanouchi [97], Morino, Kuchitsu, Takahashi and Maeda [98].
CH_2CF_2	Morino, Kuchitsu and Shimanouchi [97], Morino, Kuchitsu, Takahashi and Maeda [98].
CH_3OH	Kimura, Kimura and Shibata [85], Kimura and Kimura [80], Kimura and Kubo [81].
CH_2CCH_2 (Allene)	Cyvin [33], [34].
CD_2CCD_2 (Allene-d_4)	Cyvin [33], [34].
CCl_3CCl_3	Morino and Hirota [95].
$SiCl_3SiCl_3$	Morino and Hirota [95].
CCl_3SiCl_3	Morino and Hirota [95].
C_3H_6 (Cyclopropane)	Bastiansen and Cyvin [18].
C_6H_6 (Dimethyl-diacetylene)	Almenningen, Bastiansen and Munthe-Kaas [5].
C_6H_6 (Bensene)	Bastiansen and Cyvin [19], Cyvin [25], [35].
C_6D_6 (Bensene-d_6)	Cyvin [27], [35].
C_4H_{10} (n-butane)	Kuchitsu [87].

Table III. Values of mean amplitudes of vibration (u) from electron-diffraction and spectroscopic data, abstracted from literature.[*]

Molecule	Distance[a]	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
O_2	O-O (1.208)	0.037		(72)	0.037		(72)
Br_2	Br-Br(2.290)	0.045		(72)	0.0456 0.0457	T-300°K corr. for anharmonicity	(110)
CO_2	C-O (1.162)	0.034±0.003		(73)	0.034		(73)
	O-O (2.310)	0.040±0.007		(73)	0.041		(73)
PH_3	P-H (1.437)	0.085±0.008		(40)	0.0862		(40)
	H-H				0.1521	T-298°K	(40)
S_2Cl_2	S-S (1.97)	0.05±0.03		(44)	0.048	Approximate	(44)
	S-Cl(2.07)	0.05±0.01		(44)	0.054	"	(44)
	S-Cl(3.245)	0.08±0.02		(44)	0.087	"	(44)
	Cl-Cl(4.11)	0.14±0.07		(44)	0.158 0.257	"	(44)
S_2Br_2	S-S (1.98)	0.05	Assumed	(44)	0.048	298°K Approx.	(44)
	S-Br(2.24)	0.05±0.02		(44)	0.055	"	(44)

Table III (Continued).

Molecule	Distance[a])	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
(S_2Br_2)	$S\cdots Br(3.35)$	$0.09_8\pm 0.02$		(44)	0.092	298°K.Approx.	(44)
	$Br\cdots Br(4.26)$	0.31		(44)	0.180	"	(44)
CCl_4	$C\cdots Cl(1.767)$	$\begin{cases} 0.041\pm 0.005 \\ 0.060\pm 0.005 \\ 0.0505\pm 0.002 \end{cases}$	Refined "	(73) (15) (99)	0.053_8		(99)
	$Cl\cdots Cl(2.888)$	$\begin{cases} 0.054\pm 0.005 \\ 0.068\pm 0.003 \\ 0.0606\pm 0.001 \end{cases}$	Refined "	(73) (15) (99)	0.067_2		(99)
CH_3Cl	$C\cdots H(1.11)$	0.089 ± 0.010		(13)	0.0761	T=293°K	(43)
	$C\cdots Cl(1.784)$	0.060 ± 0.004		(13)	0.0486	"	(43)
	$H\cdots H$				0.1286	"	(43)
	$H\cdots Cl(2.38)$	0.119 ± 0.010		(13)	0.1252	"	(43)
CH_2CH_2	$C\cdots C(1.333)$	$0.043_9\pm 0.002$		(12)	0.0419		(12)
	$C\cdots H(1.084)$	$0.076_8\pm 0.003$		(12)	0.0772		(12)
	$C\cdots H(2.120)$	0.102 ± 0.006		(12)	0.0958		(12)
CF_2CF_2	$C\cdots C(1.313)$				0.0394		(97)
	$C\cdots F(1.313)$	0.064 ± 0.005		(74)	0.0430		(97)

Table III (Continued).

Molecule	Distance a)	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
(CF₂CF₂)	C··F (2.306)	0.087±0.01		(77)	0.0550		(77)
	F··F (2.204)	0.095±0.01		(77)	0.0554		(77)
	cis F··F (2.737)	0.090±0.01		(77)	0.0939		(77)
	tr. F··F (3.515)	0.114±0.01		(77)	0.0869		(77)
CH₂CF₂	C=C (1.311)			(77)	0.0409		(77)
	C-F (1.321)	0.042±0.005		(77)	0.0438		(77)
	C··F (2.335)	0.060		(77)	0.0570		(77)
	F··F (2.161)	0.060		(77)	0.0540		(77)
	C-H (1.07)			(77)	0.0707		(77)
	C··H (2.06)			(77)	0.091		(77)
	H··H			(77)	0.123		(77)
	cis H··F (2.61)			(77)	0.135		(77)
	tr. H··F (3.29)				0.094		(77)

Table III (Continued).

Molecule	Distance a)	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
CH_3OH	O–O (1.423)	0.061±0.005 0.049±0.005		(24)	0.050		(54)
	O–H (0.960)	0.075±0.020 0.078±0.015		(24)	0.069		(54)
	O–H (1.096)	0.078±0.010 0.080±0.010		(24)	0.079		(54)
	O–H (2.070)	0.096±0.010 0.099±0.01		(24)	0.104		(54)
	C–H (1.960)	0.110		(24)			
	H–H (1.78)	0.140	Assumed	(5)	0.133		(5)
CH_2CCH_2 (Allene)	C=C (1.312)	0.0390		(6)	0.0401	T=298°K *	(55)
	C–C (2.617)	0.0519		(6)	0.0451	*	(55)
	C–H (1.082)	0.0795		(6)	0.0772	*	(55)
	C–H (2.094)	0.1046		(6)	0.1015	*	(55)
	C–H (3.206)	0.1272		(6)	0.1144	*	(55)
	H–H				0.1273	*	(55)
	H–H				0.1716	*	(55)

Table III (Continued).

Molecule	Distance [a]	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
CCl₃CCl₃	O–Cl (1.78)	0.06₆		(M)	0.06	Approximate	(M)
	O–Cl	0.06₉		(M)	0.07₁	"	(M)
	Cl–Cl	0.09₄		(M)	0.07₀	"	(M)
	g. Cl–Cl	0.13₆		(M)	0.13₆	"	(M)
	tr.Cl–Cl	0.10₉		(M)	0.06₉	"	(M)
C₄H₄Cl₂ (1,4.–di–chloro–butyne)	C≡C (1.21)	0.061		(M)	0.036	Approximate	(M)
	C₁–C₂ (1.48)	0.004		(M)	0.047	"	(M)
	C₂–C₃ (2.60)	0.051	Assumed	(M)	0.051	"	(M)
	C₁···C₃ (2.60)	0.002		(M)	0.080	"	(M)
	C₁···C₄ (4.07)	0.002		(M)	0.084	"	(M)
	C₁–Cl (1.80)	0.085		(M)	0.073	"	(M)
	C₂···Cl (2.69)	0.077		(M)	0.080	"	(M)
	C₃···Cl (3.72)	0.080		(M)	0.080	"	(M)
	C₄···Cl (5.09)	0.123		(M)	0.090	"	(M)
	C₁–H (1.10)	0.077	Assumed	(M)	0.077	"	(M)
	C₂···H (2.10)	0.092		(M)	0.120	"	(M)
	C₃–H (3.18)	0.092		(M)	0.120	"	(M)

Table III (Continued).

Molecule	Distance [a]	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
$(C_4H_4Cl_2)$	$C_2\cdots H_4$ (4.63)	0.092		(34)	0.120	Approximate	(34)
	$Cl\cdots H$ (2.88)	0.088		(34)	0.114	"	(34)
	$H\cdots H$ (1.80)	0.120	Assumed	(34)	0.120	"	(34)
C_6H_6	$C_2=C_3$ (1.210)	0.040		(5)	0.036	T~310°K	(5)
(Dimethyl-	C_3-C_4 (1.379)	0.051		(5)	0.044	"	(5)
diacety-	C_1-C_2 (1.452)	0.051		(5)	0.045	"	(5)
lene)	$C_2\cdots C_4$ (2.590)	0.050		(5)	0.049	"	(5)
	$C_2\cdots C_5$ (2.661)	0.066		(5)	0.049	"	(5)
	$C_2\cdots C_6$ (3.778)	0.049		(5)	0.053	"	(5)
	$C_1\cdots C_4$ (4.026)	0.060		(5)	0.057	"	(5)
	$C_1\cdots C_5$ (5.223)	0.072		(5)	0.059	"	(5)
	$C_2\cdots C_6$ (6.661)	0.080		(5)	0.065	"	(5)
	C_1-H (1.08)	0.077		(5)	0.076	"	(5)

Table III (Continued).

Molecule	Distance a)	u (Å) El.diffr.		Note	Ref.	u (Å) Spectr.	Note	Ref.
C6H6 (Benzene)	C1—C2(1.397)	{ 0.055 b)		(44)	(21)	0.0459	T=208°K	(25)
		0.0455		(4)	(4)			
		0.0453 }		(4)	(4)			
	C1—C3(2.419)	{ 0.067 c)		(4)	(4)	0.0547		
		0.054		(4)	(4)			
		0.054 }		(4)	(4)			
	C1···C4(2.795)	{ 0.075±0.01		(4)	(4)	0.0697		(25)
		0.062		(4)	(4)			
		0.064 }		(4)	(4)			
	C1—H1(1.084)	{ 0.072±0.015		(4)	(4)	0.0771		(25)
		0.073		(4)	(4)			
		0.073 }		(4)	(4)			
	C1—H2(2.149)	{ 0.092±0.02		(4)	(4)	0.1004		(25)
		0.094		(4)	(4)			
		0.092 }		(4)	(4)			
	C1···H3(3.405)	{ 0.116	Assumed	(4)	(4)	0.0960	"	(25)
		0.094		(4)	(4)			
		0.092 }		(4)	(4)			
	C1···H4(3.881)	{ 0.135	Assumed	(4)	(4)	0.0942	"	(25)
		0.007		(4)	(4)			
		0.009 }		(4)	(4)			

Table III (Continued).

Molecule	Distance	u (Å) El.diffr.	Note	Ref.	u (Å) Spectr.	Note	Ref.
(C_6H_6)	$H_1\cdots H_2$				0.1561	$T=298°K$	[35]
	$H_1\cdots H_3$				$\left. \begin{array}{l} 0.1321 \\ \end{array} \right\} (3\pm1.2)°$	$n=3$	[24]
	$H_1\cdots H_4$				0.1191	"	[25]
C_4H_{10}	C_2-C_3	$\left. \begin{array}{l} 0.052_6 \pm 0.003 \\ 0.055_1 \pm 0.003 \end{array} \right\} (1.533)$	Defined	[37]	$\left\{ \begin{array}{l} 0.048_7 (0.040)^{d)} \\ 0.049_8 (0.049)_1 \end{array} \right.$	[1,3]	[37]
(n-butane)	C_1-C_2			[24]	$\left\{ \begin{array}{l} 0.051 (0.051) \\ 0.048_9 (0.049)_0 \end{array} \right.$		[37]
	$C_1\cdots C_3$	$\left. \begin{array}{l} 0.077_6 \pm 0.007 \\ 0.079_4 \pm 0.006 \end{array} \right\} (2.547)$	Refined	[37]	$\left\{ \begin{array}{l} 0.069_2 (0.068) \\ 0.070_4 (0.078)_2 \end{array} \right.$	H-H	[37]
	$C_1\cdots C_3$			[24]		H-H	[24]
	$s.C_1\cdots C_4$	$\left\{ \begin{array}{l} 0.136 \\ 0.109\pm0.016 \end{array} \right.$		[37]	$\left. \begin{array}{l} (0.161)_1 \\ (0.169)_1 \end{array} \right.$		[37]
		(3.072)		[24]			[24]
	$tr.C_1\cdots C_4$	$\left\{ \begin{array}{l} 0.067 \pm 0.007 \\ 0.083 \pm 0.014 \end{array} \right.$	Refined	[37]	$\left. \begin{array}{l} 0.070_4 \\ 0.079_2 \end{array} \right.$	H-H	[37]
		(3.900)		[24]			[24]
	$C-H$	$\left\{ \begin{array}{l} 0.083_1 \pm 0.004 \\ 0.078_0 \pm 0.004_8 \end{array} \right.$ (1.106)	Refined	[37]	0.078_3		[37]
							[24]

Table III (Continued).

Molecule	Distance [a]	α (Å) El.diffr.	Note	Ref.	α (Å) Spectr.	Note	Ref.
(C_4H_{10})	C-C (2.183) {	0.097 ± 0.005 Refined	[k]		0.109_7	(m)	
		0.103 ± 0.006 El.diffr.					
	C-H (2.78)	0.182 ± 0.04	(u)				
	C-H (3.60)	0.132 ± 0.05	(u)				
	H-H				0.138_8	(m)	
	tr.H-H				0.122_8	(3)	
	6. H-H				0.184_8	(m)	

*) For additional spectroscopic u-values, see Table LI.

u) The equilibrium interatomic distance values listed in parentheses are quoted from the respective electron-diffraction works. They are not intended to give accurate information, and in many cases they are not equal to the 'true' equilibrium distances. For a serious study of the equilibrium parameters, the cited papers should be consulted.

b) $0.088-\frac{1}{3}a\pm0.007$; $0 \leq a < 0.08$

c) $0.067-\frac{1}{3}b\pm0.007$, $0 \leq b < 0.05$

d) The figures in parentheses refer to the gauche form; the others to the trans form.

2. THE RIGOROUS METHOD OF CALCULATING MEAN AMPLITUDES
OF VIBRATION

2.1. Theory

The method which is going to be described in this
section is based on the assumption of small harmonic
vibrations. In spite of this approximation it is usually
referred to as the rigorous method for computing mean
amplitudes of vibration.

Diatomic molecules. The harmonic oscillator is
taken as the molecular model of a diatomic molecule,
and the Schrödinger equation yields the following result
for the eigenfunctions and the corresponding energy
values [see, e.g. reference (136)].

$$\psi_v(Q) = N \exp[-\tfrac{1}{2}\gamma Q^2] \, H_v(\gamma^{\frac{1}{2}}Q) , \qquad (2.1)$$

$$E_v = h\nu(v + \tfrac{1}{2}) , \qquad \nu = (1/2\pi)k^{\frac{1}{2}}\mu^{-\frac{1}{2}} . \qquad (2.2)$$

ν is the vibrational frequency, k the force constant and
μ the reduced mass. The normalizing factor is denoted by
N, and H_v is the Hermite polynomial. If Q denotes the
normal coordinate, the introduced constant γ is given by

$$\gamma = 4\pi^2 \nu/h . \qquad (2.3)$$

In a given vibrational state, characterized by v,
it is found for the mean value of Q^2 [see, e.g.(136)]

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$$(\overline{Q^2})_v = \int Q^2 |\psi_v|^2 \, dQ = (1/\gamma)(v + \tfrac{1}{2}) = (1/4\pi^2 \nu^2) E_v \ . \quad (2.4)$$

The quantity $\overline{Q^2}$ is determined in the following way by taking the mean of $(\overline{Q^2})_v$ over all vibrational states according to the well-known statistical distribution law.

$$\overline{Q^2} = \sum_v (\overline{Q^2})_v \exp[-\beta E_v] \Big/ \sum_v \exp[-\beta E_v]$$

$$= (1/4\pi^2 \nu^2) \sum_v E_v \exp[-\beta E_v] \Big/ \sum_v \exp[-\beta E_v]$$

$$= (h/8\pi^2 \nu) \coth(h\beta\nu/2) \ . \quad (2.5)$$

Here $\beta = 1/kT$, where k is Boltzmann's constant and T the absolute temperature.

The interatomic distance deviation, r, is proportional to the normal coordinate (Q) according to

$$r = \mu^{-\tfrac{1}{2}} Q \ . \quad (2.6)$$

Hence the mean-square amplitude of vibration (u^2) equals

$$u^2 = \overline{r^2} = \mu^{-1} \overline{Q^2} \ , \quad (2.7)$$

yielding the result

$$u^2 = \overline{r^2} = (h/8\pi^2 \mu \nu) \coth(h\beta\nu/2) \ . \quad (2.8)$$

In many cases of not extremely low frequencies the temperature-dependent factor can be omitted by computations at usual temperatures. In practice, $\coth x$ may be put

2.1.

equal to unity for $x > 4$, corresponding to approximately $\nu/c > 1600$ cm^{-1} at $T = 298$ ^{o}K. The formula (8) then reduces to

$$u^2 = \overline{r^2} = h/8\pi^2 \mu\nu , \qquad (2.9)$$

representing the mean-square amplitude of vibration in the ground state $(T = 0)$, viz. $(\overline{Q^2})_{v=0}$.

Polyatomic molecules. *) Let S denote a column matrix consisting of an arbitrary number of displacement coordinates, which very well may be a set of interatomic distance deviations. The displacements are expressed in terms of the normal coordinates of vibration by

$$S = LQ \qquad (2.10)$$

in matrix notation. Now the symbol $\overline{X}$ will be used to denote a matrix where all the elements are the mean values of the corresponding elements of X. Then the matrix

$$\overline{S\tilde{S}} = L(\overline{Q\tilde{Q}})\tilde{L} \qquad (2.11)$$

is to be considered. The mean-square values of the S coordinates appear along the main diagonal, and a specific one of them is expressed by

$$\overline{s_j^2} = \tilde{L}_j(\overline{Q\tilde{Q}})L_j . \qquad (2.12)$$

Here L_j denotes the column matrix which is composed of the coefficients L_{jk} of the expression

$$s_j = \sum_k L_{jk} \, Q_k . \qquad (2.13)$$

---

*)For the original development, see Morino, Kuchitsu and Shimanouchi[97].

2.1.

By a quantum-mechanical treatment it is found [see reference (98) and references cited therein] that $\overline{Q\tilde{Q}}$ actually is a diagonal matrix with elements of the same form as the derived expression (5) in the case of diatomic molecules, viz.

$$\overline{Q_k^2} = (h/8\pi^2\nu_k) \coth(h\beta\nu_k/2). \tag{2.14}$$

Here ν_k is the normal frequency attached to the normal coordinate Q_k. Consequently, equation (12) may be written

$$\overline{S_j^2} = \sum_k L_{jk}^2 \overline{Q_k^2} \tag{2.15}$$

or

$$\overline{S_j^2} = \sum_k L_{jk}^2 (h/8\pi^2\nu_k) \coth(h\beta\nu_k/2). \tag{2.16}$$

The most laborious part of this method is represented by the computation of the quantities L_{jk}. The generally adopted procedure, first introduced by Wilson (132), (133) may be followed, and shall be outlined in the following. *)

Now let S denote a column matrix consisting of a complete set of internal coordinates, and L the matrix which transforms the normal coordinates into the S coordinates [cf. equation (10)]. The energy matrices, viz. the potential energy matrix F and the inverse kinetic energy matrix G in terms of the S coordinates have to be constructed. **) The F matrix is built up of a set of

*) For general references to the theory of molecular vibrations, see Dennison (49),(50), Wilson (132),(133), Eliashevich (53), and (111),(55),(92),(91). For text-books, see (64),(129),(137),(136).

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force constants, the G matrix containing the masses of
the atoms and occasionally the equilibrium parameters
of the molecule in question. The following relations
involving the matrix L exist.

$$\tilde{L}FL = \Lambda, \quad \tilde{L}G^{-1}L = E, \quad L\tilde{L} = G. \quad (2.17)$$

Here Λ is a diagonal matrix with elements λ_k along the
diagonal, given by

$$\lambda_k = 4\pi^2 \nu_k^2. \quad (2.18)$$

E is the identity matrix. From the relations (17) the
homogeneous set of equations

$$(GF - \lambda_k E)L_{(k)} = O \quad (2.19)$$

is deduced, where $L_{(k)}$ represents the columns of the L
matrix. Hence the elements L_{jk} may be determined by the
standard method of characteristic vectors applied to the
GF matrix. The restriction for non-vanishing solutions
of equation (19) yields a secular equation of the form

$$|GF - \lambda E| = 0, \quad (2.20)$$

which is used for detecting the relations connecting the
normal vibrational frequencies and the force constants.

It will be profitable to chose the coordinates of
S as a set of symmetry coordinates. Then the energy mat-
rices reduce to a symmetrized form with non-vanishing
elements concentrated along the main diagonal in a manner

**) The vibrational part of the potential energy (V) and the
kinetic energy (T) may be expressed in terms of these matrices
by $2V = \tilde{S}FS$ and $2T = \dot{\tilde{S}}G^{-1}\dot{S}$.

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that can be predicted by group-theoretical considerations. The secular equation will be factorized accordingly. If the symmetry coordinates S are formed by Wilson's method as an orthogonal transformation of a set of valence force coordinates, one has

$$S = Rq \ , \qquad q = \tilde{R}S \ , \qquad (2.21)$$

where q represents the valence force coordinates and R is the transformation matrix.

To compute the mean amplitude of vibration for a given interatomic distance deviation r_i according to equation (16), the transformation coefficients of

$$r_i = \sum_k K_{ik} q_k \qquad (2.22)$$

are needed [see equation (13)]. Let a representative set of interatomic displacements between all types of atom pairs (bonded and non-bonded) of a molecule be collected in a column matrix denoted by r . To compute all the mean amplitudes of vibration, the transformation matrix K of

$$r = KQ \qquad (2.23)$$

is required. The following procedure has proved to be practically useful for computing the matrix. First the interatomic distance deviations are expressed linearly in terms of valence force coordinates from geometrical considerations, i.e. the transformation

$$r = Uq \qquad (2.24)$$

is determined. Next the displacements are expressed in

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terms of the symmetry coordinates as

$$r = VS . \tag{2.25}$$

From the transformation of equation (21) it is found

$$V = U\tilde{R} . \tag{2.26}$$

Finally the desired matrix of equation (23) is obtained from the relation

$$K = VL = (U\tilde{R})L . \tag{2.27}$$

2.2. Application to simple molecular models

It may happen that the normal frequencies of a molecule are distributed among the symmetry species so that none of them contains more than one single frequency which, however, may be degenerate. In such cases the secular equation (20) will factorize into linear equations, the symmetry coordinates will be proportional to the normal coordinates, and simple explicit expressions for the mean amplitudes of vibration may be evaluated. In the present section this sort of calculations will be reported.
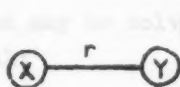

Fig.1. Diatomic molecule model. r denotes the interatomic displacement.

Diatomic molecules. The XY molecular model (Fig.1) is considered, and the symbols μ_X and μ_Y are used for the inverse masses of the X and Y atoms, respectively. The formula listed in Table IV is obtained immediately from equation (8) by substituting ($\mu_X + \mu_Y$) for

2.2.

μ^{-1}. The force constant k appearing in equation (2) is given by

$$k = \lambda(\mu_X + \mu_Y)^{-1} = 4\pi^2\nu^2(\mu_X + \mu_Y)^{-1}. \qquad (2.28)$$

By introducing k, the formula of the mean-square amplitude of vibration may be written

$$u^2 = \overline{r^2} = (h/4\pi)(\mu_X+\mu_Y)^{\frac{1}{2}}k^{-\frac{1}{2}}\coth(h\beta\nu/2). \qquad (2.29)$$

<u>Linear symmetrical XY₂ molecules.</u> *) The case of linear symmetrical XY_2 molecules (Fig.2) will be treated in some detail as an illustration of the method. Since the displacements to the first order approximation are considered, only the non-degenerate normal modes of vibration need to be taken into account, viz. the totally symmetrical vibration of frequency ν_1, and the normal vibration of frequency ν_3 belonging to the symmetry species A_{2u}. The following symmetry coordinates are formed.

$$S_1 = 2^{-\frac{1}{2}}(r_1+r_2) , \quad S_3 = 2^{-\frac{1}{2}}(r_1-r_2) . \qquad (2.30)$$

The energy matrices in terms of the valence force coordinates given on Fig.2, and the symmetry coordinates of
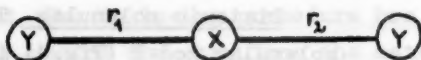

Fig.2. Linear symmetrical XY_2 molecule model ($D_{\infty h}$). The symbols r_1 and r_2 denote the respective deviations from the equilibrium X-Y distances.

*) See also references (33),(39),(40).

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equations (30) are summarized below.[*)]

$$F: \begin{array}{c} \\ r_1 \\ r_2 \end{array} \begin{array}{cc} r_1 & r_2 \\ \left[\begin{array}{cc} k & k' \\ & k \end{array}\right] \end{array} \qquad G: \begin{array}{c} \\ r_1 \\ r_2 \end{array} \begin{array}{cc} r_1 & r_2 \\ \left[\begin{array}{cc} \mu_X + \mu_Y & -\mu_X \\ & \mu_X + \mu_Y \end{array}\right] \end{array}$$

$$F: \begin{array}{c} \\ s_1 \\ s_3 \end{array} \begin{array}{cc} s_1 & s_3 \\ \left[\begin{array}{cc} k+k' & 0 \\ & k-k' \end{array}\right] \end{array} \qquad G: \begin{array}{c} \\ s_1 \\ s_3 \end{array} \begin{array}{cc} s_1 & s_3 \\ \left[\begin{array}{cc} \mu_Y & 0 \\ & 2\mu_X + \mu_Y \end{array}\right] \end{array}$$

Accordingly the linear part of the potential energy (V) is given by

$$2V = k(r_1^2 + r_2^2) + 2k'r_1 r_2 = (k+k')s_1^2 + (k-k')s_3^2 , \quad (2.31)$$

and the introduced force constants, viz. k and k' may be interpreted as the bond stretching and the bond-bond interaction constants, respectively. The secular equation gives the following relations for the frequencies or λ-values [cf. equation (18)],

$$\lambda_1 = (k+k')\mu_Y , \quad \lambda_3 = (k-k')(2\mu_X + \mu_Y) , \quad (2.32)$$

which may be solved for the force constants with the result

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[*)] The elements beneath the main diagonals of symmetric matrices are omitted.

2.2.

$$k = \tfrac{1}{2}\big[\lambda_1\mu_Y^{-1} + \lambda_3(2\mu_X+\mu_Y)^{-1}\big] ,$$
$$k' = \tfrac{1}{2}\big[\lambda_1\mu_Y^{-1} - \lambda_3(2\mu_X+\mu_Y)^{-1}\big] . \tag{2.33}$$

The connection between the symmetry coordinates and the normal coordinates is

$$S_1 = \mu_Y^{\tfrac{1}{2}}Q_1 , \qquad S_3 = (2\mu_X+\mu_Y)^{\tfrac{1}{2}}Q_3 . \tag{2.34}$$

The two types of interatomic distance deviations are represented by

$$r_{X-Y} = r_1 = 2^{-\tfrac{1}{2}}(S_1+S_3) = 2^{-\tfrac{1}{2}}\mu_Y^{\tfrac{1}{2}}Q_1 + 2^{-\tfrac{1}{2}}(2\mu_X+\mu_Y)^{\tfrac{1}{2}}Q_3 \tag{2.35}$$

and

$$r_{Y\cdots Y} = r_1 + r_2 = 2^{\tfrac{1}{2}}S_1 = 2^{\tfrac{1}{2}}\mu_Y^{\tfrac{1}{2}}Q_1 . \tag{2.36}$$

From these expressions the mean-square amplitudes of vibration, viz. $u_{X-Y}^2 = \overline{r_{X-Y}^2}$ and $u_{Y\cdots Y}^2 = \overline{r_{Y\cdots Y}^2}$ may be computed with the result listed in Table IV. By introducing the force constants from equations (31)-(33), the formulae may be written

$$u_{X-Y}^2 = (h/8\pi)\big[\mu_Y^{\tfrac{1}{2}}(k+k')^{-\tfrac{1}{2}}\coth(h\beta\nu_1/2)$$
$$+ (2\mu_X+\mu_Y)^{\tfrac{1}{2}}(k-k')^{-\tfrac{1}{2}}\coth(h\beta\nu_3/2)\big] , \tag{2.37}$$

$$u_{Y\cdots Y}^2 = (h/2\pi)\,\mu_Y^{\tfrac{1}{2}}(k+k')^{-\tfrac{1}{2}}\coth(h\beta\nu_1/2) . \tag{2.38}$$

Regular trigonal X_3 molecules. In the case of a regular trigonal X_3 molecule model (Fig.3) there are two normal vibrations, viz. the totally symmetrical one (ν_1) and one doubly degenerate (ν_2). The mean-square amplitude
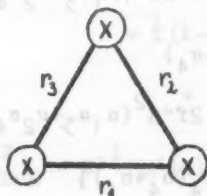
2.2.

Fig.3. Regular trigonal X_3 molecule model (D_{3h}). The symbols denote the respective interatomic displacements.

formula is given in Table IV. The complete harmonic force field is given by

$$2V = k(r_1^2+r_2^2+r_3^2) + 2k'(r_1r_2+r_2r_3+r_3r_1) .$$ (2.39)

For the force constants the following relations are deduced.

$$k = \frac{1}{3}(\lambda_1 + 4\lambda_2)\mu_X^{-1} , \qquad k' = \frac{1}{3}(\lambda_1 - 2\lambda_2)\mu_X^{-1} .$$ (2.40)

With these force constants the mean-square amplitude of vibration may be written

$$u^2 = 3^{-\frac{1}{2}}(h/4\pi)\mu_X^{\frac{1}{2}}\left[(k+2k')^{-\frac{1}{2}}\coth(h\beta\nu_1/2)\right.$$
$$\left. + 2^{\frac{1}{2}}(k-k')^{-\frac{1}{2}}\coth(h\beta\nu_2/2)\right] .$$ (2.41)

<u>Plane square X_4 molecules.</u>[*]) The frequencies of the four in-plane normal vibrations of this molecular model (Fig.4) are denoted by ν_1 (symmetry species A_{1g}), ν_2 (B_{1g}), ν_3 (B_{2g}) and ν_5 (E_u). The respective mean-square amplitudes of vibration for the bonded and non-bonded XX distances are listed in Table IV. Let the in-plane part of the potential function be given by

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*) See also reference [106].

2.2.

$$2V = k(r_1^2+r_2^2+r_3^2+r_4^2) + 2k'(r_1+r_3)(r_2+r_4) + 2k''(r_1r_3+r_2r_4)$$
$$+ fR^2(\alpha_1^2+\alpha_2^2+\alpha_3^2+\alpha_4^2) + 2f'R^2(\alpha_1+\alpha_3)(\alpha_2+\alpha_4)$$
$$+ 2f''R^2(\alpha_1\alpha_3+\alpha_2\alpha_4)$$
$$+ 2gR[r_1(\alpha_1+\alpha_2)+r_2(\alpha_2+\alpha_3)+r_3(\alpha_3+\alpha_4)+r_4(\alpha_4+\alpha_1)]$$
$$+ 2g'R[r_1(\alpha_3+\alpha_4)+r_2(\alpha_4+\alpha_1)+r_3(\alpha_1+\alpha_2)+r_4(\alpha_2+\alpha_3)] .$$

(2.42)

The following relations exist for the force constants,

$$k+k'' = \tfrac{4}{4}(\lambda_1 + \lambda_2)\mu_X^{-1} , \qquad k' = \tfrac{4}{8}(\lambda_1 - \lambda_2)\mu_X^{-1} ,$$
$$f-2f'+f'' = \tfrac{4}{8}\lambda_3\mu_X^{-1} ,$$

(2.43)

$$k-k''+2(f-f'')-4(g-g') = \tfrac{1}{2}\lambda_5\mu_X^{-1} ,$$

and the mean-square amplitudes of vibration may be expressed in the following way.
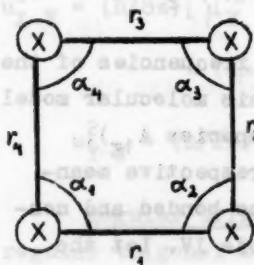

Fig.4. Plane square X_4 molecule model (D_{4h}). The symbols denote the respective deviations from the equilibrium bond distances and inter-bond angles. The equilibrium length of the X-X distance is denoted by R.

2.2.

$$u^2_{X-X} = 2^{-\frac{1}{2}}(h/4\pi)\mu_X^{\frac{1}{2}}\left\{\tfrac{1}{2}(k+2k'+k'')^{-\frac{1}{2}}\coth(h\beta\nu_1/2)\right.$$

$$+ \tfrac{1}{2}(k-2k'+k'')^{-\frac{1}{2}}\coth(h\beta\nu_2/2)$$

$$\left. + [k-k''+2(f-f'')-4(g-g')]^{-\frac{1}{2}}\coth(h\beta\nu_3/2)\right\}, \quad (2.44)$$

$$u^2_{X\cdots X} = 2^{-\frac{1}{2}}(h/4\pi)\mu_X^{\frac{1}{2}}\left[(k+2k'+k'')^{-\frac{1}{2}}\coth(h\beta\nu_1/2)\right.$$

$$\left. + \tfrac{1}{2}(f-2f'+f'')^{-\frac{1}{2}}\coth(h\beta\nu_3/2)\right] . \quad (2.45)$$

<u>Tetrahedral X_4 molecules.</u>[*] The notation used for the
frequencies of the normal
vibrations of tetrahedral
X_4 molecules (Fig.5) is
as follows: ν_1 for the
non-degenerate frequency,
ν_2 for the doubly degene-
rate and ν_3 for the triply
degenerate frequency. The
mean-square amplitude of
vibration is given in
Table IV. The complete
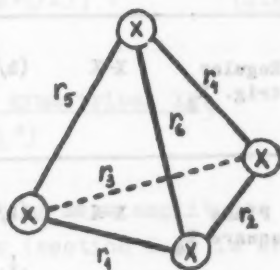harmonic force field is
given by

Fig.5. Tetrahedral X_4 molecule
model (T_d). The symbols denote
interatomic displacements.

$$2V = k(r_1^2+r_2^2+r_3^2+r_4^2+r_5^2+r_6^2) + 2k'[(r_1+r_4)(r_2+r_3+r_5+r_6)$$

$$+(r_2+r_5)(r_3+r_6)] + 2k''(r_1r_4+r_2r_5+r_3r_6) . \quad (2.46)$$

For the force constants of this equation one has

_____

*) See also references [117],[105],[35],[29].

2.2.

Table IV. Mean-square amplitudes of vibration of simple molecular models.I.

Molecule	Distance	Mean-square amplitude of vibration
Diatomic	X–Y	$(h/8\pi^2 \nu)(\mu_X + \mu_Y)\coth(h\beta\nu/2)$
Linear sym.XY$_2$	X–Y	$(h/16\pi^2)[\mu_Y \nu_1^{-1} \coth(h\beta\nu_1/2)$ $+ (2\mu_X + \mu_Y)\nu_3^{-1} \coth(h\beta\nu_3/2)]$
	Y··Y	$(h/4\pi^2\nu_1)\mu_Y \coth(h\beta\nu_1/2)$
Regular trig. X$_3$	X–X	$(h/8\pi^2)\mu_X[\nu_1^{-1} \coth(h\beta\nu_1/2)$ $+ \nu_2^{-1}\coth(h\beta\nu_2/2)]$
Plane square X$_4$	X–X	$(h/8\pi^2)\mu_X[\tfrac{1}{2}\nu_1^{-1} \coth(h\beta\nu_1/2)$ $+\tfrac{1}{2}\nu_2^{-1}\coth(h\beta\nu_2/2) + \nu_5^{-1}\coth(h\beta\nu_5/2)]$
	X··X	$(h/8\pi^2)\mu_X[\nu_1^{-1} \coth(h\beta\nu_1/2)$ $+ \nu_3^{-1} \coth(h\beta\nu_3/2)]$
Tetra-hedral X$_4$	X–X	$(h/8\pi^2)\mu_X[\tfrac{2}{3}\nu_1^{-1} \coth(h\beta\nu_1/2)$ $+\tfrac{1}{3}\nu_2^{-1}\coth(h\beta\nu_2/2) + \nu_3^{-1}\coth(h\beta\nu_3/2)]$

2.2.

$$k = \frac{1}{24}(\lambda_1 + 8\lambda_2 + 6\lambda_3)\mu_X^{-1} \ ,$$

$$k' = \frac{1}{24}(\lambda_1 - 4\lambda_2)\mu_X^{-1} \ , \qquad (2.47)$$

$$k'' = \frac{1}{24}(\lambda_1 + 8\lambda_2 - 6\lambda_3)\mu_X^{-1} \ ,$$

and the mean-square amplitude of vibration may be put in the form

$$u^2 = (h/4\pi)\mu_X^{\frac{1}{2}}\left[\ \frac{1}{3}(k+4k'+k'')^{-\frac{1}{2}}\coth(h\beta\nu_1/2)\right.$$

$$+ \frac{1}{3}(k-2k'+k'')^{-\frac{1}{2}}\coth(h\beta\nu_2/2)$$

$$\left. + 2^{-\frac{1}{2}}(k-k'')^{-\frac{1}{2}}\coth(h\beta\nu_3/2)\right] \ . \qquad (2.48)$$

2.3. Application to the plane symmetrical XY_3 molecular model *)

The rigorous method of computing mean amplitudes of vibration described in this chapter (section 2.1) is now going to be applied to the plane symmetrical XY_3 molecular model. The normal-coordinate analysis will be carried out in details, and numerical calculations for boron tri-fluoride will be reported.

Molecular symmetry. Much information concerning molecular vibrations is obtained from group-theoretical considerations. The considered molecular model (Fig.6) belongs to the symmetry group D_{3h}, and the characters of the irreducible representations of this group are given in Table V [see, e.g.,[136]]. The table also includes the characters (χ) of two reducible representations and the respective symmetrical structures (n). The former one, with the characters denoted by χ_Q, is obtained when a

---

*) See also references [126],[104],[38],[34].

2.3.

complete set of internal coordinates is taken as the
basis of the representation. The corresponding symmetric
structure, given by the numbers n_Q, may be written in a
symbolic way as

$$\Gamma(Q) = A_1' + 2E' + A_2'' \tag{2.49}$$

and shows how the normal vibrations are distributed among
the symmetry species. The latter reducible representation
is obtained when one of the following symmetric equivalent
sets are taken as the basis: (i) The bond displacements
r_1, r_2 and r_3, (ii) the angle displacements α_1, α_2 and α_3,
or (iii) the three non-bonded distance deviations r^*. One
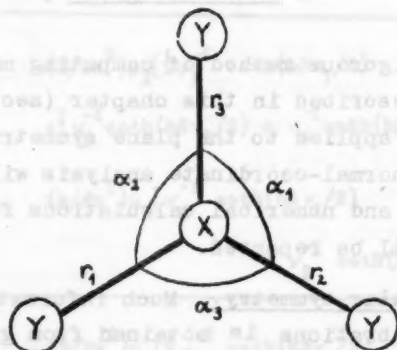of the normal vibrations, viz. that of species A_2'', is an

Fig.6. Notation used for the plane symmetrical XY_3 molecular
model (D_{3h}). The symbols denote the deviations from the
equilibrium distances and angles. r^* represents the inter-
atomic Y··Y displacements of a non-bonded atom pair. The
equilibrium length of the X—Y bond is denoted by R.

2.3.

Table V. Characters (χ) and symmetrical structures (n) for some representations of the symmetry group D_{3h}.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	n_Q	$n_r, n_\alpha, n_{r'}$
A_1'	1	1	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1	0	0
E'	2	-1	0	2	-1	0	2	1
A_1''	1	1	1	-1	-1	-1	0	0
A_2''	1	1	-1	-1	-1	1	1	0
E''	2	-1	0	-2	1	0	0	0
	6	0	0	4	-2	2	χ_Q	
	3	0	1	3	0	1	$\chi_r, \chi_\alpha, \chi_{r'}$	

out-of-plane motion. Since the present treatment is based on the assumption of small harmonic vibrations, only the in-plane vibrations need to be considered.

The six r and α coordinates represent a set of in-plane valence force coordinates, where one redundant condition is involved. A set of in-plane symmetry coordinates may be formed as linear combinations of the valence force coordinates. The following expressions have been evaluated.

Symm.species A_1': $\qquad S_1 = 3^{-\frac{1}{2}}(r_1 + r_2 + r_3)$,

Symm.species E_a': $\qquad \begin{cases} S_{3a} = 6^{-\frac{1}{2}}(2r_1 - r_2 - r_3) , \\ S_{4a} = 6^{-\frac{1}{2}}R(2\alpha_1 - \alpha_2 - \alpha_3) , \end{cases}$ (2.50)

Symm.species E_b': $\qquad \begin{cases} S_{3b} = 2^{-\frac{1}{2}}(r_2 - r_3) , \\ S_{4b} = 2^{-\frac{1}{2}}R(\alpha_2 - \alpha_3) . \end{cases}$

2.3.

A complete, orthogonal and normalized set is obtained if the following redundant coordinate is added to these coordinates.

$$S_r = 3^{-\frac{1}{2}} R(\sigma_1 + \alpha_2 + \alpha_3) \equiv 0 . \tag{2.51}$$

It should be noticed that the angle deviations α have been multiplied by the bond length R.

Energy matrices. The in-plane part of the potential energy function in terms of the coordinates of the types r and Rα defines a set of force constants, given by the **F** matrix. The elements of the corresponding **G** matrix may be determined by means of tabulated formulae (47),(134). These matrices are given in the following.

$$
\mathbf{F}:\quad
\begin{array}{c}
r_1 \\ r_2 \\ r_3 \\ R\alpha_1 \\ R\alpha_2 \\ R\alpha_3
\end{array}
\begin{array}{cccccc}
r_1 & r_2 & r_3 & R\alpha_1 & R\alpha_2 & R\alpha_3 \\
\left[\begin{array}{cccccc}
k & k' & k' & g & g' & g' \\
 & k & k' & g' & g & g' \\
 & & k & g' & g' & g \\
 & & & f & f' & f' \\
 & & & & f & f' \\
 & & & & & f
\end{array}\right]
\end{array}
$$

$$
\mathbf{G}:\quad
\begin{array}{c}
r_1 \\ r_2 \\ r_3
\end{array}
\begin{array}{ccc}
r_1 & r_2 & r_3 \\
\left[\begin{array}{ccc}
\mu_X+\mu_Y & -\tfrac{1}{2}\mu_X & -\tfrac{1}{2}\mu_X \\
 & \mu_X+\mu_Y & -\tfrac{1}{2}\mu_X \\
 & & \mu_X+\mu_Y
\end{array}\right.
\end{array}
\begin{array}{ccc}
R\sigma_1 & R\sigma_1 & R\sigma_3 \\
\left.\begin{array}{ccc}
3^{\frac{1}{2}}\mu_X & -\tfrac{1}{2}3^{\frac{1}{2}}\mu_X & -\tfrac{1}{2}3^{\frac{1}{2}}\mu_X \\
 & 3^{\frac{1}{2}}\mu_X & -\tfrac{1}{2}3^{\frac{1}{2}}\mu_X \\
 & & 3^{\frac{1}{2}}\mu_X
\end{array}\right]
\end{array}
$$

2.3.

$$
G : \quad
\begin{array}{c}
 \\
R\alpha_1 \\
R\alpha_2 \\
R\alpha_3
\end{array}
\begin{array}{ccc}
R\sigma_1 & R\sigma_2 & R\sigma_3 \\
\left[\begin{array}{ccc}
3\mu_X+2\mu_Y & -\tfrac{1}{2}(3\mu_X+2\mu_Y) & -\tfrac{1}{2}(3\mu_X+2\mu_Y) \\
 & 3\mu_X+2\mu_Y & -\tfrac{1}{2}(3\mu_X+2\mu_Y) \\
 & & 3\mu_X+2\mu_Y
\end{array}\right]
\end{array}
$$

The form of the s y m m e t r i z e d F and G matrices is deducible by group-theoretical considerations. According to equation (49), they will consist of a one-dimensional block for the coordinate of species A_1', and two identical two-dimensional blocks for the degenerate pair of coordinates of the species E'. The elements of the energy matrices in terms of the chosen symmetry coordinates have been evaluated by means of the transformation given by equations (50), and are specified below.

Symm. species A_1'

Symm. species E'

$$
F : \quad
\begin{array}{c}
S_1 \\
\\
S_3 \\
S_4
\end{array}
\begin{array}{c}
S_1 \\
\big[\, k+2k' \,\big]
\end{array}
\qquad
\begin{array}{cc}
S_3 & S_4 \\
\left[\begin{array}{cc}
k-k' & g-g' \\
 & f-f'
\end{array}\right]
\end{array}
$$

Symm. species A_1'

Symm. species E'

$$
G : \quad
\begin{array}{c}
S_1 \\
\\
S_3 \\
S_4
\end{array}
\begin{array}{c}
S_1 \\
\big[\, \mu_Y \,\big]
\end{array}
\qquad
\begin{array}{cc}
S_3 & S_4 \\
\left[\begin{array}{cc}
\tfrac{1}{2}(3\mu_X+2\mu_Y) & \tfrac{1}{2}3^{\tfrac{1}{2}}\mu_X \\
 & \tfrac{1}{2}(3\mu_X+2\mu_Y)
\end{array}\right]
\end{array}
$$

2.3.

Normal frequencies. The secular equation yields
the following expressions for the normal vibrational
frequencies ($\Lambda = 4\pi^2\nu^2$).

$$\Lambda_1 = K_1\mu_Y,$$

$$\Lambda_3+\Lambda_4 = \tfrac{1}{2}(K_2+3\phi)(3\mu_X+2\mu_Y) + 3^{\tfrac{1}{2}}\Gamma\mu_X, \qquad (2.52)$$

$$\Lambda_3\Lambda_4 = 3(K_2\phi - \Gamma^2)(3\mu_X+\mu_Y)\mu_Y.$$

In these equations K_1, K_2, ϕ and Γ are the force
constants of the symmetrized potential energy matrix,
i.e.

$$K_1 = k+2k', \quad K_2 = k-k', \quad \phi = f-f', \quad \Gamma = g-g'. \quad (2.53)$$

Interatomic distance deviations. The two types of
interatomic distance deviations are represented by

$$r = r_1, \quad r^* = \tfrac{1}{2}3^{\tfrac{1}{2}}(r_2+r_3) + \tfrac{1}{2}Ra_1. \quad (2.54)$$

These quantities in terms of the symmetry coordinates are
expressed by the linear combinations

$$r = 3^{-\tfrac{1}{2}}S_1 + \tfrac{1}{3}6^{\tfrac{1}{2}}S_3, \quad r^* = S_1 - 2^{-\tfrac{1}{2}}S_3 + 6^{-\tfrac{1}{2}}S_4. \quad (2.55)$$

Numerical computations for boron trifluoride. To
determine the complete harmonic force field of a molecule
of the considered type, a further piece of information is
needed in addition to the normal frequencies of the mole-
cule. In the present work the complete in-plane harmonic
force field for boron trifluoride has been determined from
the frequencies ν_1, ν_3 and ν_4 for $^{11}BF_3$, together with
the additional frequency ν_3 for $^{10}BF_3$. For the numerical
values, see Table VI. [For other calculations, see (62),
(65), (126), (88), (131), (104).]

2.3.

Table VI. Experimental vibrational frequencies and calculated force constants of boron trifluorides.

		Fundamental frequencies (cm^{-1}) [a]	
Species	No.	$^{11}BF_3$	$^{10}BF_3$
A_1'	1	888	888
E'	3	1453.5	1504.7
	4	480.4	482.0

Force constants (mdyne $Å^{-1}$)			
K_1	8.8236	k	7.8791
K_2	7.4068	k'	0.4723
ϕ	0.50013	$f-f'$	0.50013
Γ	-0.63980	$g-g'$	-0.63980

[a]) From reference ([68]); observed fundamentals.

Table VII. Coefficients of transformations involving normal coordinates for $^{11}BF_3$ in $(Awu)^{-\frac{1}{2}}$ units.

	Q_1	Q_3	Q_4
S_1	0.22942	...	...
S_3	...	0.43455	0.0013308
S_4	...	0.54129	0.52299
r	0.13245	0.35481	0.0010866
r^*	0.22942	-0.086294	0.21257

2.3.

Table VIII. Mean amplitudes of vibration in $^{11}BF_3$.

Distance	Mean amplitude in Å	
	T-0	298 °K
B-F	0.0424	0.0425
F-F	0.0517	0.0552

The symmetry coordinates and subsequently the interatomic distance deviations for boron trifluoride of the ^{11}B isotope have been expressed as linear combinations of the normal coordinates (Q). The numerical values of the coefficients are given in Table VII.

Finally the mean amplitudes of vibration were calculated at the temperatures 0 and 298 °K, and are listed in Table VIII.

2.4. Application to the cyclopropane molecular model [*]

In this section the nine-atomic cyclopropane model $(XYY')_3$ is studied. The case is found to be appreciably more complicated than that of the previous section, but still the rigorous method is practically applicable.

Molecular symmetry. The cyclopropane molecular model (Fig.7) belongs to the symmetry group D_{3h} in its equilibrium position, which is determined by the following structural parameters: (i) The equilibrium X-X distance, denoted by D; (ii) the X-Y distance, R, and (iii) the equilibrium YXY' angle, 2A. The equilibrium value of the XXY angle is identified with the symbol B. The following connections exist between the quantities A and B.

$$\cos A = -\tfrac{2}{3}3^{\frac{1}{2}}\cos B , \quad \cos 2A = \tfrac{1}{3}(5 - 8\sin^2 B) . \quad (2.56)$$

The character table of the actual group is shown

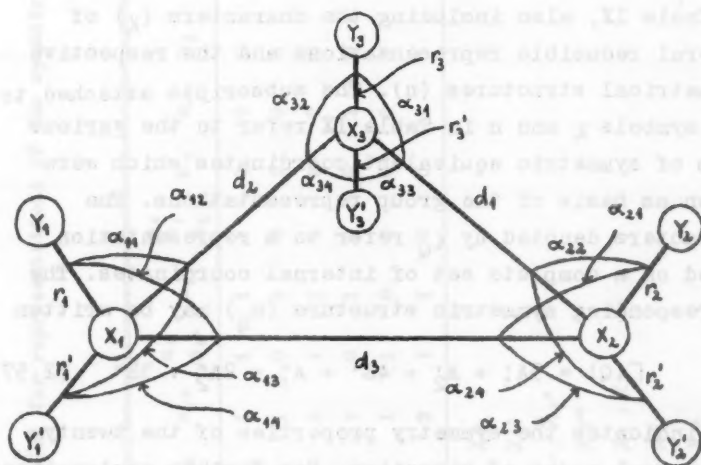[*] See also reference (136) pp. 137-140, and reference (57).

2.4.

Fig.7. Notation used for the cyclopropane molecular model
X_3Y_6 (D_{3h}). **The symbols denote deviations from the equilibrium distances and angles.**

In addition, the following symbols are adopted (i = 1, 2,3).

$$\zeta_i = \tfrac{1}{2}(\alpha_{i1} + \alpha_{i2} + \alpha_{i3} + \alpha_{i4}) \; ; \text{ deformation,}$$

$$\eta_i = \tfrac{1}{2}(\alpha_{i1} - \alpha_{i2} + \alpha_{i3} - \alpha_{i4}) \; ; \text{ wagging,}$$

$$\vartheta_i = \tfrac{1}{2}(\alpha_{i1} - \alpha_{i2} - \alpha_{i3} + \alpha_{i4}) \; ; \text{ twisting,}$$

$$\xi_i = \tfrac{1}{2}(\alpha_{i1} + \alpha_{i2} - \alpha_{i3} - \alpha_{i4}) \; ; \text{ rocking.}$$

r^* denotes the displacement for a X···Y or X···Y' distance between non-bonded X and Y atoms,

t represents the Y···Y' displacements for a pair of Y atoms attached to the same X atom,

t^* represents the Y···Y and Y'···Y' displacements, and

t^{**} represents the Y···Y' displacements at different X atoms.

2.4.

in Table IX, also including the characters (χ) of several reducible representations and the respective symmetrical structures (n). The subscripts attached to the symbols χ and n in Table IX refer to the various sets of symmetric equivalent coordinates which were taken as basis of the group representations. The characters denoted by χ_Q refer to a representation based on a complete set of internal coordinates. The corresponding symmetric structure (n_Q) may be written

$$\Gamma(Q) = 3A_1' + A_2' + 4E' + A_1'' + 2A_2'' + 3E'' \qquad (2.57)$$

and indicates the symmetry properties of the twenty-one normal modes of vibration. For further explanations of the adopted symbols references are made to Fig.7 and the adherent text.

A complete set of symmetry coordinates has been formed as given by the following expressions.

Species A_1':
$$\begin{cases} S_1 = 6^{-\frac{1}{2}}(r_1+r_2+r_3+r_1'+r_2'+r_3') , \\ S_2 = 3^{-\frac{1}{2}}(d_1+d_2+d_3) , \\ S_3 = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\zeta_1+\zeta_2+\zeta_3) , \end{cases}$$

Species A_2':
$$S_4 = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\eta_1+\eta_2+\eta_3) ,$$

Species E_a':
$$\begin{cases} S_{5a} = 12^{-\frac{1}{2}}(2r_1-r_2-r_3+2r_1'-r_2'-r_3') , \\ S_{6a} = 6^{-\frac{1}{2}}(2d_1-d_2-d_3) , \\ S_{7a} = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\zeta_1-\zeta_2-\zeta_3) , \\ S_{8a} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\eta_2-\eta_3) , \end{cases}$$

Table IX. Characters (χ) and symmetrical structures (n) for representations of the symmetry group D_{3h}.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	n_a	$n_{r'}$	n_r	n_t n_i $n_{i'}$	n_{i} $n_{t'}$ $n_{t''}$	$n_{t'}$	n_t	
A_1'	1	1	1	1	1	1	8	1	1	1	0	1	0	χ_r
A_2'	1	1	-1	1	1	-1	1	1	0	0	1	0	0	$\chi_{r'}$
E'	2	-1	0	2	-1	0	4	2	1	1	0	1	1	$\chi_r, \chi_{t'}$
A_1''	1	1	1	-1	-1	-1	1	1	0	0	1	0	0	$\chi_{t''}$
A_2''	1	1	-1	-1	-1	1	1	1	1	0	0	1	0	$\chi_t, \chi_{t'}, \chi_t$
E''	2	-1	0	-2	1	0	3	2	1	1	1	1	1	$\chi_r, \chi_{t'}, \chi_t$

2.4.

Species E_b':
$$
\begin{cases}
S_{5b} = \tfrac{1}{2}(r_2 - r_3 + r_2' - r_3') \ , \\
S_{6b} = 2^{-\frac{1}{2}}(d_2 - d_3) \ , \\
S_{7b} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\zeta_2 - \zeta_3) \ , \\
S_{8b} = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(-2\eta_1 + \eta_2 + \eta_3) \ ,
\end{cases}
$$

Species A_1'':
$$
S_9 = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\vartheta_1 + \vartheta_2 + \vartheta_3) \ ,
$$

Species A_2'':
$$
\begin{cases}
S_{10} = 6^{-\frac{1}{2}}(r_1 + r_2 + r_3 - r_1' - r_2' - r_3') \ , \\
S_{11} = 3^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\xi_1 + \xi_2 + \xi_3) \ ,
\end{cases}
$$

Species E_a'':
$$
\begin{cases}
S_{12a} = 12^{-\frac{1}{2}}(2r_1 - r_2 - r_3 - 2r_1' + r_2' + r_3') \ , \\
S_{13a} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\vartheta_2 - \vartheta_3) \ , \\
S_{14a} = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\xi_1 - \xi_2 - \xi_3) \ ,
\end{cases}
$$

Species E_b'':
$$
\begin{cases}
S_{12b} = \tfrac{1}{2}(r_2 - r_3 - r_2' + r_3') \ , \\
S_{13b} = 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(-2\vartheta_1 + \vartheta_2 + \vartheta_3) \ , \\
S_{14b} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\xi_2 - \xi_3) \ .
\end{cases}
\tag{2.58}
$$

__Potential energy matrix.__ By symmetry considerations
the complete harmonic potential field is found to be
described by twenty-seven force constants. The following
symbols are applied: k for a bond stretching force cons-
tant or a bond-bond interaction, f for an angle deforma-
tion (including wagging, twisting and rocking) or angle-
angle interaction constant divided by RD, and g for a
bond-angle interaction constant divided by $(RD)^{\frac{1}{2}}$. The
form of the potential energy function in terms of the
chosen internal coordinates, viz. r, d, and the given
combinations of the α's multiplied by $(RD)^{\frac{1}{2}}$ (see Fig.
7), may be deduced from Table X. Let for instance the

2.4.

Table X. Force constants of the complete harmonic force field of a cyclopropane type molecule. [a])

	r_1	r_2	r_3	r_1'	r_2'	r_3'
r_1	k_r	k_r''	k_r'''	k_r''	k_r'''	k_r'''

	d_1	d_2	d_3	$\rho\zeta_1$	$\rho\zeta_2$	$\rho\zeta_3$
r_1	k_{rd}	k_{rd}'	k_{rd}'	$g_{r\zeta}$	$g_{r\zeta}'$	$g_{r\zeta}'$
d_1	k_d	k_d'	k_d'	$g_{d\zeta}$	$g_{d\zeta}'$	$g_{d\zeta}'$
$\rho\zeta_1$				f_ζ	f_ζ'	f_ζ'

	$\rho\eta_1$	$\rho\eta_2$	$\rho\eta_3$	$\rho\vartheta_1$	$\rho\vartheta_2$	$\rho\vartheta_3$	$\rho\xi_1$	$\rho\xi_2$	$\rho\xi_3$
r_1	0	$g_{r\eta}'$	$-g_{r\eta}'$	0	$g_{r\vartheta}'$	$-g_{r\vartheta}'$	$g_{r\xi}'$	$g_{r\xi}'$	$g_{r\xi}'$
r_1'	0	$g_{r\eta}'$	$-g_{r\eta}'$	0	$g_{r\vartheta}'$	$-g_{r\vartheta}'$	$g_{r\xi}'$	$g_{r\xi}'$	$g_{r\xi}'$
d_1	0	$g_{d\eta}'$	$-g_{d\eta}'$	0	0	0	0	0	0
$\rho\zeta_1$	0	$f_{\zeta\eta}'$	$-f_{\zeta\eta}'$	0	0	0	0	0	0
$\rho\eta_1$	f_η	f_η'	f_η'	0	0	0	0	0	0
$\rho\vartheta_1$				f_ϑ	f_ϑ'	f_ϑ'	$f_{\vartheta\xi}'$	$f_{\vartheta\xi}'$	$-f_{\vartheta\xi}'$
$\rho\xi_1$							$2f_\xi'$	f_ξ'	f_ξ'

[a]) $\rho = (RD)^{\frac{1}{2}}$.

force constant corresponding to the term $(RD)^{\frac{1}{2}} r_2' \eta_3$ be wanted. By the symmetry operation C_3^2 the considered product is transformed to $(RD)^{\frac{1}{2}} r_1' \eta_2$, hence the desired force constant is found to be $g_{r\eta}'$ in the applied notation.

2.4.

In addition to the constants of Table X the force constants attached to the valence angle coordinates α (see Fig. 7) are tabulated in a similar manner in Table XI. The connection between the two sets of angle deformation and angle-angle interaction constants is given by Wilson, Decius and Cross [reference (134), p. 139]. In the present notation it may be written

$$
\begin{aligned}
f_\zeta &= a + b + c + d, & f_\zeta' &= e + g + \tfrac{1}{2}(f+h+i+j), \\
f_\eta &= a - b + c - d, & f_\eta' &= e + g - \tfrac{1}{2}(f+h+i+j), \\
f_\vartheta &= a - b - c + d, & f_\vartheta' &= e - g - \tfrac{1}{2}(f-h+i-j), \\
f_\xi &= a + b - c - d, & f_\xi' &= e - g + \tfrac{1}{2}(f-h+i-j), \\
f_{\zeta\eta}' &= -\tfrac{1}{2}(f+h-i-j), & f_{\vartheta\xi}' &= \tfrac{1}{2}(f-h-i+j).
\end{aligned} \tag{2.59}
$$

For completeness the corresponding expressions containing the bond-angle interaction constants are given in the following.

$$
\begin{aligned}
g_{r\zeta} &= k + l, & g_{r\zeta}' &= \tfrac{1}{2}(m+n+p+q), \\
g_{r\xi} &= k - l, & g_{r\xi}' &= \tfrac{1}{2}(m+n-p-q), \\
g_{r\eta}' &= \tfrac{1}{2}(m-n+p-q), & g_{r\vartheta}' &= \tfrac{1}{2}(m-n-p+q), \\
g_{d\zeta}' &= 2r, \quad g_{d\xi}' = s + t, & g_{d\eta}' &= s - t.
\end{aligned} \tag{2.60}
$$

The potential energy matrix in terms of the symmetry coordinates is given in Table XII. The two degenerate sets of coordinates belonging to the species E' and E" contribute with identical blocks to the matrix in accordance with the theory. For brevity only one block of each species is included in the table.

Table XI. Force constants for the terms involving valence angle displacements of a cyclopropane type molecule. a)

	$\varphi\alpha_{11}$	$\varphi\alpha_{12}$	$\varphi\alpha_{13}$	$\varphi\alpha_{14}$	$\varphi\alpha_{21}$	$\varphi\alpha_{22}$	$\varphi\alpha_{23}$	$\varphi\alpha_{24}$	$\varphi\alpha_{31}$	$\varphi\alpha_{32}$	$\varphi\alpha_{33}$	$\varphi\alpha_{34}$
r_1	k	l	l	l	m	n	m	n	n	n	q	p
r_1'	l	k	r	r	p	q	p	q	q	t	n	m
d_1	r	r	d	d	s	t	s	t	t	t	q	n
$\varphi\alpha_{11}$	a	a	e	c	a	e	a	h	e	e	g	j
$\varphi\alpha_{12}$	d	c	b	o	i	e	j	e	f	f	h	i
$\varphi\alpha_{13}$	b	d	a	b	g	h	e	f	g	g	e	l
$\varphi\alpha_{14}$	a	a	e	a	j	g	l	e	h	i	e	e

a) $\gamma = (RD)^{\frac{1}{2}}$.

2.4.

Table XII. The symmetrized potential energy matrix for the cyclopropane molecular model.

		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
Species A_1'	S_1	K_r	K_{rd}	$\Gamma_{r\zeta}$					
	S_2		K_d	$\Gamma_{d\zeta}$					
	S_3			Φ_ζ					
Species A_2'	S_4				Φ_η				
Species E'	S_5					K_r'	K_{rd}'	$\Gamma_{r\zeta}'$	$\Gamma_{r\eta}'$
	S_6						K_d'	$\Gamma_{d\zeta}'$	$\Gamma_{d\eta}'$
	S_7							Φ_ζ'	$\Phi_{\zeta\eta}'$
	S_8								Φ_η'

		S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}
Species A_1''	S_9	Φ_ω''					
Species A_2''	S_{10}		K_r'	$\Gamma_{r\xi}''$			
	S_{11}			Φ_ξ''			
Species E''	S_{12}				K_r''	$\Gamma_{r\omega}'''$	$\Gamma_{r\xi}'''$
	S_{13}					Φ_ω'''	$\Phi_{\omega\xi}'''$
	S_{14}						Φ_ξ'''

$$K_r = k_r + k_r' + 2k_r'' + 2k_r'''$$

$$K_r' = k_r + k_r' - k_r'' - k_r'''$$

$$K_r'' = k_r - k_r' + 2k_r'' - 2k_r'''$$

$$K_r''' = k_r - k_r' - k_r'' + k_r'''$$

$$K_d = k_d + 2k_d'$$

$$K_d' = k_d - k_d'$$

$$K_{rd} = 2^{\frac{1}{2}}(k_{rd} + 2k_{rd}')$$

$$K_{rd}' = 2^{\frac{1}{2}}(k_{rd} - k_{rd}')$$

2.4.

Table XII (Continued).

$$\Phi_\zeta = f_\zeta + 2f'_\zeta \qquad\qquad \Phi_\eta = f_\eta + 2f'_\eta$$

$$\Phi'_\zeta = f_\zeta - f'_\zeta \qquad\qquad \Phi'_\eta = f_\eta - f'_\eta$$

$$\Phi''_{\not\!\partial} = f_{\not\!\partial} + 2f'_{\not\!\partial} \qquad\qquad \Phi''_\xi = f_\xi + 2f'_\xi$$

$$\Phi'''_{\not\!\partial} = f_{\not\!\partial} - f'_{\not\!\partial} \qquad\qquad \Phi'''_\xi = f_\xi - f'_\xi$$

$$\Phi'_{\zeta\eta} = 3^{\frac{1}{2}} f'_{\zeta\eta} \qquad\qquad \Phi'''_{\not\!\partial\xi} = -3^{\frac{1}{2}} f'_{\not\!\partial\xi}$$

$$\Gamma_{r\zeta} = 2^{\frac{1}{2}}(g_{r\zeta} + 2g'_{r\zeta}) \qquad\qquad \Gamma_{d\zeta} = g_{d\zeta} + 2g'_{d\zeta}$$

$$\Gamma'_{r\zeta} = 2^{\frac{1}{2}}(g_{r\zeta} - g'_{r\zeta}) \qquad\qquad \Gamma'_{d\zeta} = g_{d\zeta} - g'_{d\zeta}$$

$$\Gamma'_{r\eta} = 6^{\frac{1}{2}} g'_{r\eta} \qquad\qquad \Gamma'_{d\eta} = 3^{\frac{1}{2}} g'_{d\eta}$$

$$\Gamma'''_{r\not\!\partial} = 6^{\frac{1}{2}} g'_{r\not\!\partial} \qquad\qquad \Gamma''_{r\xi} = 2^{\frac{1}{2}}(g_{r\xi} + 2g'_{r\xi})$$

$$\Gamma'''_{r\xi} = 2^{\frac{1}{2}}(g_{r\xi} - g'_{r\xi})$$

Inverse kinetic energy matrix. The elements of
the inverse kinetic energy matrix in terms of the chosen
internal coordinates (Fig. 7) have been constructed by
means of tabulated formulae (47), (136), and are given in
Table XIII. The corresponding G matrix has the same
form as the F matrix composed of the elements from Table
X, disregarded from the fact that some more of the G
matrix elements vanish.

The elements of the G matrix in terms of the
symmetry coordinates are given in Table XIV.

In Tables XIII and XIV the following abbreviations
have been applied.

2.4.

Table XIII. Elements of the inverse kinetic energy matrix for the cyclopropane molecular model. [a])

	r_1	r_2	r_1'	r_2'	d_1	d_2
r_1	$\mu_X + \mu_Y$	0	$\mu_X \cos 2A$	0	0	$\mu_X \cos B$
d_1					$2\mu_X$	$-\tfrac{1}{2}\mu_X$

$$\rho\zeta_1$$

r_1	$-\tfrac{1}{3}\left[(D/R)^{\frac{1}{2}} S\cos B + (R/D)^{\frac{1}{2}} C\right]\mu_X \sin B$
d_1	$(R/D)^{\frac{1}{2}}\mu_X \cot B$
$\rho\zeta_1$	$\left[(D/R)(\tfrac{1}{3} S\mu_X \sin^2 B + \tfrac{1}{2}\mu_Y) + \tfrac{2}{3}\mu_X \cos B\right] S + (R/D) C\mu_X$

$$\rho\zeta_2$$

r_1	$\tfrac{1}{3}(R/D)^{\frac{1}{2}} C\mu_X \sin B$
d_1	$-\tfrac{1}{2}\left[(D/R)^{\frac{1}{2}} S\sin B + (R/D)^{\frac{1}{2}} \cot B\right]\mu_X$
$\rho\zeta_1$	$-\left[\tfrac{1}{3} S\cos B + \tfrac{1}{2}(R/D) C\right]\mu_X$

$$\rho\eta_1$$

r_1	0
d_1	0
$\rho\zeta_1$	0
$\rho\eta_1$	$\left[(D/R)(\mu_X + \tfrac{1}{2}\mu_Y) - 2\mu_X \cos B\right](1/\sin^2 B) + \tfrac{5}{3}(R/D) C\mu_X$

2.4.

Table XIII (Continued).

	$\rho\eta_2$
r_1	$\frac{1}{3}(R/D)^{\frac{1}{2}}C\mu_X\sin B$
d_1	$\frac{1}{2}[(D/R)^{\frac{1}{2}} - (R/D)^{\frac{1}{2}}\cos B](\mu_X/\sin B)$
$\rho\zeta_1$	$[\frac{2}{3}\cos B - \frac{1}{4}(R/D)]C\mu_X$
$\rho\eta_1$	$-[(\cot B/\sin B) - \frac{7}{6}(R/D)C]\mu_X$

	$\rho\vartheta_1$	$\rho\vartheta_2$
r_1	0	$\frac{1}{3}(R/D)^{\frac{1}{2}}S\mu_X\sin B$
d_1	0	0
$\rho\zeta_1$	0	0
$\rho\eta_1$	0	0
$\rho\vartheta_1$	$\frac{1}{2}(D/R)(\mu_Y/\sin^2 B) + \frac{2}{3}(R/D)S\mu_X$	$-\frac{4}{3}(R/D)S\mu_X$

	$\rho\xi_1$
r_1	$\frac{2}{3}[(D/R)^{\frac{1}{2}}\cos B - (R/D)^{\frac{1}{2}}]S\mu_X\sin B$
d_1	0
$\rho\zeta_1$	0
$\rho\eta_1$	0
$\rho\vartheta_1$	0
$\rho\xi_1$	$\{(D/R)(\frac{4}{3}\mu_X\cos^2 B + \frac{1}{2}\mu_Y) - 2[\frac{4}{3}\cos B - (R/D)]\mu_X\}S$

2.4.

Table XIII (Continued).

	$\rho\xi_2$
r_1	$\frac{1}{2}(R/D)^{\frac{1}{2}}S\mu_X\sin B$
d_1	0
$\rho\zeta_1$	0
$\rho\eta_1$	0
$\rho\vartheta_1$	$-[\frac{2}{3}\cos B - (R/D)]S\mu_X$
$\rho\xi_1$	$[\frac{4}{3}\cos B - (R/D)]S\mu_X$

a) $\rho = (RD)^{\frac{1}{2}}$, $C = (1/\sin^2 B) - 1$, $S = -[(1/\sin^2 B) - 4]$.

$$C = (1/\sin^2 B) - 1 = \frac{3}{4}\cos^2 A/\sin^2 B ,$$
$$S = -[(1/\sin^2 B) - 4] = 3\sin^2 A/\sin^2 B. \tag{2.61}$$

μ_X and μ_Y denote as usual the inverse masses of the X and Y atoms, respectively.

Interatomic distances. In cyclopropane there are six types of interatomic distances. The notation for the deviations from the equilibrium distances is given by Fig. 7 with the **added text**. The equilibrium lengths are denoted by the corresponding capital letters. For the non-bonded distances it is found

$$R^* = (R^2 + D^2 - 2RD\cos B)^{\frac{1}{2}} ,$$
$$T = 2R\sin A , \qquad T^* = D - 2R\cos B , \tag{2.62}$$
$$T^{**} = [4R^2(1-\frac{1}{3}\cos^2 B) + D^2 - 4RD\cos B]^{\frac{1}{2}}.$$

Table XIV. Tabulation of the symmetrized inverse kinetic energy matrix of the cyclopropane molecular model. a)

	S_1	S_2	S_3
S_1	$2\mu_X\cos^2 A + \mu_Y$	$2^{\frac{1}{2}}\mu_X\cos B$	$-\frac{1}{2}2^{\frac{1}{2}}(D/R)^{\frac{1}{2}}S\mu_X\sin 2B$
S_2		$3\mu_X$	$-(D/R)^{\frac{1}{2}}S\mu_X\sin B$
S_3			$\frac{1}{2}(D/R)(2\mu_X\sin^2 A + \mu_Y)S$

A_1' (rows S_1, S_2, S_3)

	S_4
S_4	$[(D/R)(\mu_X + \frac{1}{2}\mu_Y) - 4\mu_X\cos B](1/\sin^2 B) + 4(D/R)C\mu_X$

A_2'

	S_5	S_6	S_7
S_5	$2\mu_X\cos^2 A + \mu_Y$	$-2^{\frac{1}{2}}\mu_X\cos B$	$-2^{\frac{1}{2}}[\frac{1}{3}(D/R)^{\frac{1}{2}}S\cos B + (R/D)^{\frac{1}{2}}C]\mu_X\sin B$
S_6		$\frac{1}{2}\mu_X$	$\frac{1}{2}[(D/R)^{\frac{1}{2}}S\sin B + 3(R/D)^{\frac{1}{2}}\cot B]\mu_X$
S_7			$[\frac{1}{2}(D/R)(2\mu_X\sin^2 A + \mu_Y) + \mu_X\cos B]S + \frac{1}{2}(R/D)C\mu_X$

E' (rows S_5, S_6, S_7)

2.4.

Interatomic distance deviations. A representative set of six interatomic displacements in the cyclopropane molecular model has been expressed linearly in terms of the introduced internal coordinates (see Fig. 7) with the following result.

(X_1-Y_1) $\quad r = r_1$,

$(X_3\cdots Y_1)$ $\quad r^* = (1/R^*)\big[(R-DcosB)r_1 + (D-RcosB)d_2$
$$\qquad\qquad\qquad + \tfrac{1}{2}RDsinB(\zeta_1+\eta_1+\vartheta_1+\xi_1)\big]$$,

(X_2-X_3) $\quad d = d_1$,

$(Y_1\cdots Y_1')$ $\quad t = sinA(r_1+r_1') - \tfrac{1}{3}(R/D)(cos^2A/sinA)(2d_1-d_2-d_3)$
$$\qquad\qquad\qquad + \tfrac{2}{3}R(sin2B/sinA)\,\zeta_1$$,

$(Y_2\cdots Y_3)$ $\quad t^* = -cosB(r_2+r_3) + d_1$
$$\qquad\qquad + \tfrac{1}{2}RsinB(\zeta_2+\zeta_3-\eta_2+\eta_3-\vartheta_2+\vartheta_3+\xi_2+\xi_3)$$,

$(Y_2\cdots Y_3')$ $\quad t^{**} = (1/T^{**})\big\{\big[2R(1-\tfrac{1}{3}cos^2B) - DcosB\big](r_2+r_3')$
$$\qquad + (D-2RcosB)d_1 + \tfrac{2}{3}(R^2/D)cos^2B(2d_1-d_2-d_3)$$
$$\qquad + \tfrac{1}{2}RsinB(D+\tfrac{2}{3}RcosB)(\zeta_2+\zeta_3+\xi_2-\xi_3)$$
$$\qquad - \tfrac{1}{2}RsinB(D-2RcosB)(\eta_2-\eta_3+\vartheta_2+\vartheta_3)\big\}.$$

$$(2.63)$$

The same quantities are going to be expressed in terms of the symmetry coordinates. From Table IX it may be stated a priori which of the symmetry species contribute to a given interatomic displacement. As an example, only some symmetry coordinates from A_1', E', A_1'' and E'' will contribute to the coordinate t^{**}. The following expressions have been deduced.

2.4.

$$r = 6^{-\frac{1}{2}}S_1 + 3^{-\frac{1}{2}}S_{5a} + 6^{-\frac{1}{2}}S_{10} + 3^{-\frac{1}{2}}S_{12a} \, ,$$

$$r^* = (1/R^*)\big[6^{-\frac{1}{2}}(R-D\cos B)S_1 + 3^{-\frac{1}{2}}(D-R\cos B)S_2$$
$$+ 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(S_3+S_4)\sin B$$
$$+ 3^{-\frac{1}{2}}(R-D\cos B)S_{5a} - 6^{-\frac{1}{2}}(D-R\cos B)(S_{6a}-3^{\frac{1}{2}}S_{6b})$$
$$+ 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(S_{7a}-S_{8b}+2^{-\frac{1}{2}}S_9)\sin B$$
$$+ 6^{-\frac{1}{2}}(R-D\cos B)S_{10} + 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}S_{11}\sin B$$
$$+ 3^{-\frac{1}{2}}(R-D\cos B)S_{12a} - 6^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(S_{13b}-S_{14a})\sin B\big] \, ,$$

$$d = 3^{-\frac{1}{2}}S_2 + \tfrac{1}{2}6^{\frac{1}{2}}S_{6a} \, ,$$

$$t = \tfrac{1}{3}6^{\frac{1}{2}}S_1\sin A + \tfrac{2}{3}3^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(\sin 2B/\sin A)S_3$$
$$+ \tfrac{2}{3}3^{\frac{1}{2}}S_{5a}\sin A - \tfrac{1}{3}6^{\frac{1}{2}}(R/D)(\cos^2 A/\sin A)S_{6a}$$
$$+ \tfrac{1}{3}6^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(\sin 2B/\sin A)S_{7a} \, ,$$

$$t^* = -\tfrac{1}{3}6^{\frac{1}{2}}S_1\cos B + 3^{-\frac{1}{2}}S_2 + 3^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}S_3\sin B$$
$$+ 3^{-\frac{1}{2}}S_{5a}\cos B + \tfrac{1}{2}6^{\frac{1}{2}}S_{6a} - 6^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(S_{7a}+3^{\frac{1}{2}}S_{8a})\sin B$$
$$- \tfrac{1}{3}6^{\frac{1}{2}}S_{10}\cos B + 3^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}S_{11}\sin B$$
$$+ 3^{-\frac{1}{2}}S_{12a}\cos B - 6^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(3^{\frac{1}{2}}S_{13a}+S_{14a})\sin B \, ,$$

$$t^{**} = (1/T^{**})\Big\{ \tfrac{1}{3}6^{\frac{1}{2}}[2R(1-\tfrac{1}{3}\cos^2 B)-D\cos B]S_1$$
$$+ 3^{-\frac{1}{2}}(D-2R\cos B)S_2$$
$$+ 3^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}\sin B(D+\tfrac{2}{3}R\cos B)S_3$$
$$- 3^{-\frac{1}{2}}[2R(1-\tfrac{1}{3}\cos^2 B)-D\cos B]S_{5a}$$
$$+ \tfrac{1}{3}6^{\frac{1}{2}}[D-2R\cos B+\tfrac{2}{3}(R^2/D)\cos^2 B]S_{6a}$$
$$- 6^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}\sin B(D+\tfrac{2}{3}R\cos B)S_{7a}$$
$$- (R/D)^{\frac{1}{2}}\sin B(D-2R\cos B)(2^{-\frac{1}{2}}S_{8a}+3^{-\frac{1}{2}}S_9)$$
$$+ [2R(1-\tfrac{1}{3}\cos^2 B)-D\cos B]S_{12b}$$

2.4.

$$- 6^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}\sin B(D-2R\cos B)S_{13b}$$
$$+ 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}\sin B(D+\tfrac{2}{3}R\cos B)S_{14b} \Big\} \ .$$

$$(2.64)$$

Experimental data for cyclopropane and cyclo-
propane-d_6. Cyclopropane molecules have been subjected
to many spectroscopic investigations, some of the most
recent ones being reported by Baker and Lord [9],
Günthard, Lord and McCubbin [57], and Mathai, Shepherd
and Welsh [90].

The observed fundamental frequencies used in the
present calculations are given in Table XV, and partially
taken from reference [9] (infrared data for the gaseous
state and some Raman data for the liquid phase), and
from reference [90] (Raman data for the gaseous state).

For the equilibrium parameters, the following
data have been adopted *)

(C-H, C-D)   R = 1.089 Å ,
(C-C)   D = 1.509 Å ,
(CCH, CCD)   B = 113.64° .

The corresponding YXY' (HCH or DCD) angle is 2A =
124.84° .

Introductory remarks to the calculations. In the
paper of Günthard, Lord and McCubbin [57] a vibrational
analysis is given, including the calculations of force
constants for cyclopropane. It should be noted that the
F and **G** matrices of the cited paper [57] are not directly
comparable with those of the present work, because of the

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*) Almenningen, A., Bastiansen, O., Fernholt, L. and Skancke,
   P.N. (Unpublished)

2.4.

Table XV. Observed fundamental frequencies for cyclopropane and cyclopropane-d6.

Species	No.[a]	Fundamentals (cm^{-1})	
		C$_3$H$_6$ (gas) Raman[b]	C$_3$D$_6$ (liquid) Raman[c]
A$_1'$ {	1 (Q$_1$)	3038.0	2236
	3 (Q$_2$)	1188.0	956
	2 (Q$_3$)	1479[d]	—
		C$_3$H$_6$ (gas) Infrared[c]	C$_3$D$_6$
A$_2'$	5 (Q$_4$)	963	—
		C$_3$H$_6$ (gas) Infrared[c]	C$_3$D$_6$ (gas) Infrared[c]
E' {	8 (Q$_5$)	3028.1	2211.4
	10 (Q$_6$)	1028.7	855.9
	9 (Q$_7$)	1441.8	1074.3
	11 (Q$_8$)	868.5	720.1
		C$_3$H$_6$ (gas) Raman[b]	C$_3$D$_6$
A$_1''$	4 (Q$_9$)	1132.5	—
		C$_3$H$_6$ (gas) Infrared[c]	C$_3$D$_6$ (gas) Infrared[c]
A$_2''$ {	6 (Q$_{10}$)	3102.9	2336
	7 (Q$_{11}$)	854	614

2.4.

Table XV (Continued).

		C_3H_6 (gas) Raman [b]	C_3D_6 (liquid) Raman [c]
E"	12 (Q_{12})	3082.2	2329
	13 (Q_{13})	1188.0	-
	14 (Q_{14})	738.8	528

[a]) The adopted numbering of frequencies is the same as that of the papers of Lord et al.[9],[57]. The present numbering of coordinates is somewhat different, as seen from the normal coordinates listed in parentheses.

[b]) Reference [90].

[c]) Reference [9].

[d]) Estimated from a combination band [90].

different choises of symmetry coordinates. Apart from such differences, the two sets of force constants still differ for the following reasons: (a) The calculations of the mentioned paper [57] are based on liquid phase fundamentals. In the present work, the fundamentals for the gaseous state are used when available. (b) Slightly different approximations have been assumed by the estimations of anharmonicity constants in the two cases. (c) The equilibrium data here reported are newer and somewhat different from those used by Günthard, Lord and McCubbin, viz. R = 1.08 Å, D = 1.535 Å, 2A = 118°. (d) Somewhat different approximations have been introduced in the reducing of the number of unknown force constants.

2.4.

Estimation of the normal frequencies for cyclo-
propane and cyclopropane-d$_6$. The normal frequencies (ω)
were computed from the fundamentals (ν) by means of
approximately estimated anharmonicity constants (x),
following the method proposed by Dennison [50]. The an-
harmonicity constants are defined by the equation

$$\nu_i = (1 - x_i)\,\omega_i \ . \tag{2.65}$$

Let the quantities for the deuterated molecule (C_3D_6)
be identified by an asterisk. If the approximate
assumption

$$x_i/x_i^* = \nu_i/\nu_i^* \tag{2.66}$$

is made, one finds [50], [58]

$$|G|^{\frac{1}{2}}/|G^*|^{\frac{1}{2}} = \prod_i (\omega_i/\omega_i^*) =$$

$$\prod_i [(\nu_i/\nu_i^*) - x_i]/(1-x_i) \ . \tag{2.67}$$

The observed and theoretical product rule ratios
are given in Table XVI. Notice that the C-H and C-D
stretching frequencies are separated from the remaining
frequencies in each of the species A_1', E', A_2'' and E''.

The C-H and C-D stretching frequencies (ω_1, ω_6, ω_8,
ω_{12}). The high frequencies for the C-H and C-D
stretchings were separated from the lower frequencies
according to the method developed by Wilson [133], [136].

2.4.

Table XVI. Product rule for the frequencies of cyclopropane
and cyclopropane-d_6.

Species	Frequency Nos.	Observed [a] $\Pi(\nu_i/\nu_i^*)$	Theoretical $\Pi(\omega_i/\omega_i^*)$
A_1'	1	1.3587	1.3898
	2,3	(1.4380)	1.4380
A_2'	5	(1.2381)	1.2424
E'	8	1.3693	1.3898
	9,10,11	1.8775	1.9010
A_1''	4	(1.4054)	1.4137
A_2''	6	1.3283	1.3379
	7	1.3909	1.3968
E''	12	1.3234	1.3379
	13,14	(1.7373)	1.7517

[a])Figures in parentheses involve calculated fundamentals.

Hence equations (66) and (67) were sufficient for the
determination of the normal frequencies ω_1, ω_6, ω_8 and
ω_{12}, together with the respective anharmonicity cons-
tants. The results are given in Table XVII.
The lower frequencies of species A_1' (ω_2, ω_3). For the
C_2D_6 frequencies of this species (see Table XV) the
Raman data for the liquid phase had to be uded, because
of the lack of gas frequencies. The literature (9) con-
tains also a value for the ν_2^* frequency, viz. 1270 cm^{-1},

2.4.

Table XVII. Fundamentals (ν), anharmonicity constants (x), and
normal frequencies (ω) for cyclopropane and cyclopropane–d$_6$.

Species	No.[a])	Description	Cyclopropane, C_3H_6		
			$\nu(cm^{-1})$	x [b])	$\omega(cm^{-1})$
A_1'	1 (Q_1)	CH stretching	3038.0	0.07975	3301.3
	3 (Q_2)	Ring deformation	1188.0	0.00000[c])	1188.0
	2 (Q_3)	CH$_2$ deformation	1479	0.00000[c])	1479
A_2'	5 (Q_4)	CH$_2$ wagging	963	0.01800[c])	980.7
E'	8 (Q_5)	CH stretching	3028.1	0.05246	3195.7
	10 (Q_6)	Ring deformation	1028.7	0.02088[d])	1050.6
	9 (Q_7)	CH$_2$ deformation	1441.8	0.02457	1478.1
	11 (Q_8)	CH$_2$ wagging	868.5	0.01785[d])	884.3
A_1''	4 (Q_9)	CH$_2$ twisting	1132.5	0.02000[c])	1155.6
A_2''	6(Q_{10})	CH stretching	3102.9	0.02856	3194.1
	7(Q_{11})	CH$_2$ rocking	854	0.01482	866.0
E"	12(Q_{12})	CH stretching	3082.2	0.04305	3220.8
	13(Q_{13})	CH$_2$ twisting	1188.0	0.02000[c])	1212.2
	14(Q_{14})	CH$_2$ rocking	738.8	0.01480[c])	749.9

Species	No.[a])	Description	Cyclopropane–d$_6$, C_3D_6		
			$\nu(cm^{-1})$	x [b])	$\omega(cm^{-1})$
A_1'	1 (Q_1)	CD stretching	2236	0.05870	2375.4
	3 (Q_2)	Ring deformation	956	0.00000[d])	956
	2 (Q_3)	CD$_2$ deformation	1278.1[d])	0.00000[d])	1278.1

2.4.

Table XVII (Continued).

A_2'	5 (Q_4)	CD_2 wagging	777.8[d])	0.01454[d])	789.3
E'	8 (Q_5)	CD stretching	2211.4	0.03831	2299.5
	10 (Q_6)	Ring deformation	886.9	0.01800[c])	903.2
	9 (Q_7)	CD_2 deformation	1074.3	0.01831	1094.3
	11 (Q_8)	CD_2 wagging	720.1	0.01480[c])	730.9
A_1''	4 (Q_9)	CD_2 twisting	805.8[d])	0.01423[d])	817.5
A_2''	6 (Q_{10})	CD stretching	2336	0.02150	2387.3
	7 (Q_{11})	CD_2 rocking	614	0.01066	620.6
E"	12 (Q_{12})	CD stretching	2329	0.03253	2407.3
	13 (Q_{13})	CD_2 twisting	956.8[d])	0.01611[d])	972.5
	14 (Q_{14})	CD_2 rocking	528	0.01058[d])	533.6

[a]) See footnote [a]) of Table XV.

[b]) Approximate computations. All of the reported decimals are not significant.

[c]) Assumed.

[d]) Calculated.

which is corrected for Fermi resonance. Together with this value, the separated product rule for ν_2 and ν_3 (cf. Table XVI) is almost accurately fulfilled. In the present computations both of the anharmonicity constants were assumed exactly equal to zero, and the value 1278.1 cm^{-1} for ν_2' was calculated.

2.4.

The lower frequency of species A_2'' (ω_7). The given values of x and ω (Table XVII) for the lower frequency of the species A_2'' both in C_3H_6 and C_3D_6 were calculated without further assumptions.

The lower frequencies of species E'' (ω_{13}, ω_{14}). Here again the Raman data for liquid C_3D_6 had to be used. The anharmonicity constants x_{13} and x_{14} were assumed as given in Table XVII, according to the experience that they usually are positive and increase with increasing frequencies [58]. The frequencies ν_6^* and ν_7 of the species A_2'' were used as a guide for this purpose. The calculated value 956.8 cm^{-1} for ν_{13}^* may be accepted in spite of the reported value 835 cm^{-1} [9]. This frequency has been estimated from a combination band and is rather doubtful.

The lower frequencies of species E' (ω_9, ω_{10}, ω_{11}). The x_{11}^* anharmonicity constant was assumed equal to x_{14} because of the approximately equal magnitudes of the respective frequencies. With the additional assumption of $x_{10}^* = 0.01800$ all the desired quantities could be calculated, and are found in Table XVII.

Species A_2' and A_1'' containing one frequency each (ω_5, ω_4). The x_5 anharmonicity constant, corresponding to the CH$_2$ wagging frequency of species A_2', was assumed equal to $x_{10}^* = 0.01800$. At the same time it appeared to have the same order of magnitude as the anharmoncitiy constant x_{11}, corresponding to a frequency which also has been assigned to CH$_2$ wagging. As for the A_1'' species, the assumtion $x_4 = x_{13} = 0.02000$ was made, where x_{13} corresponds to a frequency having been assigned to CH$_2$ twisting. The calculated fundamental 805.8 cm^{-1} for

2.4.

ν_4^* is quite compatible with the reported value 800 cm^{-1} (^{9}), as estimated from a combination band.

Calculation of force constants for cyclopropane. The normal frequencies (ω) given in Table XVII were used for determining the force constants of cyclopropane molecules. By these calculations, the approximate separations of the C-H and C-D frequencies were carried through, except for the species A_2''.

In the course of the force constant calculations, one preferable set was easily selected from the different solutions of the quadratic equations involved in the calculations.

Species A_1'. The approximate separation of the C-H and C-D stretching frequencies involves the assumption of two interaction constants, viz. K_{rd} and $\Gamma_{r\zeta}$, equal to zero. All the remaining force constants of this species could be calculated from the normal frequencies of both C_3H_6 and C_3D_6. The result is given in Table XVIII.

Species A_2'. This species contains only one symmetry coordinate, the corresponding force constant being included in Table XVIII.

Species E'. The separation of the C-H and C-D stretching frequencies of this species gave the value for K_r' given in Table XVIII, and three interaction force constants equal to zero. For the six remaining force constants, five independent equations (two of the first degree, two of the second degree, and one of the third degree) were available. To decrease the number of unknowns, only one additional assumption was made, namely

2.4.

Table XVIII. Force constants for cyclopropane (see Table XII).

Species	Symbol	Force constant (mdyne $Å^{-1}$)
A_1'	K_r	6.2457
	K_d	3.9500
	Φ_ζ	0.60922
	K_{rd}	0 [a]
	$\Gamma_{d\zeta}$	0.32655
	$\Gamma_{r\zeta}$	0 [a]
A_2'	Φ_η	0.48749
E'	K_r'	5.8528
	K_d'	4.3563
	Φ_ζ'	0.61795
	Φ_η'	0.70958
	K_{rd}'	0 [a]
	$\Gamma_{d\zeta}'$	−0.16327
	$\Phi_{\zeta\eta}'$	0.0443
	$\Gamma_{r\zeta}'$	0 [a]
	$\Gamma_{d\eta}'$	−0.5090
	$\Gamma_{r\eta}'$	0 [a]
A_1''	Φ_ϑ''	0.96038
A_2''	K_r''	5.3542
	Φ_ξ''	0.22223
	$\Gamma_{r\xi}''$	0.02652
E''	K_r'''	5.4411
	Φ_ϑ'''	0.60731
	Φ_ξ'''	0.19728
	$\Gamma_{r\vartheta}'''$	0 [a]

2.4.

Table XVIII (Continued).

(E")	$\Phi'''_{\vartheta\zeta}$	-0.08777
	$\Gamma'''_{r\xi}$	0 [a]

[a]) **Assumed.**

$$r = \tfrac{1}{2}g_{d\zeta} = 0 . \qquad (2.68)$$

[Cf. Tables X and XI, and equation (60)]. Hence the force constant $\Gamma'_{d\zeta}$ could be obtained by means of the value for $\Gamma_{d\zeta}$, this constant belonging to the species A'_1. The values of the remaining five constants, viz. K'_d, Φ'_ζ, Φ'_η, $\Phi'_{\zeta\eta}$ and $\Gamma'_{d\eta}$ were evaluated by a laborious iteration process started with $\Phi'_{\zeta\eta} = 0$. The final results are found in Table XVIII.

Species A''_1. This species contains only one symmetry coordinate, and the respective force constant given in Table XVIII.

Species A''_2. The normal frequencies for both C_3H_6 and C_3D_6 supply sufficient information for determining all the force constants of this species. For the numerical results, see Table XVIII.

If the separation of the C-H and C-D frequencies is carried out also in this species, the following force constants in mdyne A^{-1} are obtained:

$$K''_r = 5.3513,$$

$$\Phi''_\xi = 0.22222,$$

$$\Gamma''_{r\xi} = 0 \text{ (assumed)}.$$

2.4.

Table XIX. Force constants for cyclopropane (see Tables X and XI).

Description [a])	Symbol	Force constant (mdyne Å^{-1})
CH stretching	k_r	5.6979
CH–CH interaction	k_r'	0.28580
CH⋯CH interaction	k_r''	0.05100
CH⋯CH interaction	k_r'''	0.07999
CC stretching	k_d	4.2208
CC–CC interaction	k_d'	−0.13542
CH–CC interaction	k_{rd}	0 [b])
CH–CC interaction	k_{rd}'	0 [b])
CH_2 deformation (ζ)	f_ζ	0.61504
$\zeta⋯\zeta$ interaction	f_ζ'	−0.00291
CH_2 wagging (η)	f_η	0.63555
$\eta⋯\eta$ interaction	f_η'	−0.07403
CH_2 twisting (ϑ)	f_ϑ	0.72500
$\vartheta⋯\vartheta$ interaction	f_ϑ'	0.11769
CH_2 rocking (ξ)	f_ξ	0.20560
$\xi⋯\xi$ interaction	f_ξ'	0.00832
$\zeta⋯\eta$ interaction	$f_{\zeta\eta}'$	0.02558
$\vartheta⋯\xi$ interaction	$f_{\vartheta\xi}'$	0.05067
CH str.–CH_2 def.	$g_{r\zeta}$	0 [b])
CH str.⋯CH_2 def.	$g_{r\zeta}'$	0 [b])
CC str.–CH_2 def.	$g_{d\zeta}$	0 [b])
CC str.⋯CH_2 def.	$g_{d\zeta}'$	0.16327
CH str.⋯CH_2 wagging	$g_{r\eta}'$	0 [b])
CC str.–CH_2 wagging	$g_{d\eta}'$	−0.29387
CH str.⋯CH_2 twisting	$g_{r\vartheta}'$	0 [b])

2.4.

Table XIX (Continued).

CH str.-CH$_2$ rocking	g_{rt}		0 [b])
CH str.-CH$_2$ rocking	g'_{rt}		0 [b])
CCH bending	a		0.54530
CCH-CCH interaction	b		−0.13498
CCH-CCH interaction	c		0.08000
CCH-CCH interaction	d		0.12472
CCH-CCH interaction	e		0.01227
CCH-CCH interaction	f		0.00298
CCH-CCH interaction	g		−0.05074
CCH-CCH interaction	h		0.00700
CCH-CCH interaction	i		−0.02211
CCH-CCH interaction	j		0.08325
CH-CCH interaction	k		0.00313
CH-CCH interaction	l		−0.00313
CH-CCH interaction	m		0.00313
CH-CCH interaction	n		0.00313
CH-CCH interaction	p		−0.00313
CH-CCH interaction	q		−0.00313
CC-CCH interaction	r		0 [c])
CC-CCH interaction	s		−0.06530
CC-CCH interaction	t		0.22857

[a]) Formulated for the C$_3$H$_6$ molecule. Throughout this column the H symbols may be replaced by D. The precise definition of the symbols is given in Tables X and XI.

[b]) From assumed values.

[c]) Assumed.

2.4.

The very good agreement with the more rigorous values
included in Table XVIII leads one to beleive with confi-
dence that the approximate separation of the high
frequencies in the other cases (i.e. in species A_1', E'
and E") is justified as well.

Species E". Here again the force constants could be
determined from the C_3H_6 and C_3D_6 normal frequencies,
after separation of the high frequencies.

Further computations. The force constants given in
Table X are based on the initially chosen set of internal
coordinates, and are linearly dependent on the force
constants of the symmetrized potential energy matrix
(see Table XII). Their numerical values are given in
Table XIX, as well as those of the previously introduced
force constants involving the CCH (or CCD) valence angle
displacements. One should not attache too much signifi-
cance to the values for many of the interaction force
constants, because of their dependence on the special
assumptions made here. In particular, all of the cons-
tants m, n, p and q would be exactly equal to zero, if
the approximate separation of the high C-H and C-D
frequencies of all of the symmetry species, including
A_2'', was carried through.

Determination of the normal coordinates for cyclo-
propane and cyclopropane-d_6. The transformation matrix
L connecting the chosen symmetry coordinates and the
normal coordinates ($S = LQ$), has been determined by the
standard method of characteristic vectors. The elements
of this matrix, both for C_3H_6 and C_3D_6, are given
numerically in Table XX.

2.4.

Table XX. Tabulation of the L matrix elements for cyclopropane and cyclopropane-d_6 in $(\text{Awu})^{-\frac{1}{2}}$ units.

Cyclopropane, C_3H_6

(C_3H_6)		Q_1	Q_2	Q_3	Q_4
A_1'	S_1	1.0137	0	0	
	S_2	0	0.42651	-0.24357	
	S_3	0	0.25840	1.4523	
A_2'	S_4				1.0779

(C_3H_6)		Q_5	Q_6	Q_7	Q_8
E'	S_5	1.0137	0	0	0
	S_6	0	0.12365	0.057633	-0.32276
	S_7	0	-0.064846	1.4485	-0.0019874
	S_8	0	1.0003	0.032289	0.020045

(C_3H_6)		Q_9	Q_{10}	Q_{11}
A_1''	S_9	0.90495		
A_2''	S_{10}		1.0596	-0.0021769
	S_{11}		-0.087113	1.4114

(C_3H_6)		Q_{12}	Q_{13}	Q_{14}
E''	S_{12}	1.0596	0	0
	S_{13}	0	0.79001	0.58649
	S_{14}	0	-1.2576	1.0904

2.4.

Table XX (Continued).

Cyclopropane-d$_6$, C$_3$D$_6$

(C$_3$D$_6$)		Q$_1$	Q$_2$	Q$_3$	Q$_4$
A$'_1$	S$_1$	0.72943	0	0	
	S$_2$	0	0.16607	−0.45339	
	S$_3$	0	0.75516	0.79568	
A$'_2$	S$_4$				0.86754

(C$_3$D$_6$)		Q$_5$	Q$_6$	Q$_7$	Q$_8$
E$'$	S$_5$	0.72943	0	0	0
	S$_6$	0	0.30195	0.13377	−0.10814
	S$_7$	0	−0.20627	1.0432	0.041479
	S$_8$	0	0.55241	0.070012	0.53164

(C$_3$D$_6$)		Q$_9$	Q$_{10}$	Q$_{11}$
A$''_1$	S$_9$	0.64014		
A$''_2$	S$_{10}$		0.79199	0.0014717
	S$_{11}$		−0.12231	1.0101

(C$_3$D$_6$)		Q$_{12}$	Q$_{13}$	Q$_{14}$
E$''$	S$_{12}$	0.79199	0	0
	S$_{13}$	0	0.59600	0.43379
	S$_{14}$	0	−1.0766	0.74803

2.4.

Computations of the mean amplitudes of vibration
in cyclopropane and cyclopropane-d$_6$. The next step in
the mean amplitude computations is to express the six
representative interatomic displacements [see equations
(63)] in terms of the normal coordinates. The **V** matrix,
connecting the interatomic displacements and the symmetry

Table XXI. Contributions from normal coordinates to
interatomic displacements (K matrix elements) in cyclopropane
and cyclopropane-d$_6$ in (Amu)$^{-\frac{1}{2}}$.

(C$_3$H$_6$)	Cyclopropane, C$_3$H$_6$		
	r	r*	d
Q$_1$	0.41886	0.32065	0
Q$_2$	0	0.25918	0.24624
Q$_3$	0	0.10003	-0.14063
Q$_4$		0.16711	
Q$_{5a}$	0.58528	0.45347	0
Q$_{6a}$	0	-0.059138	0.10096
Q$_{7a}$	0	0.29666	0.047057
Q$_{8a}$	0	0.11682	-0.26354
Q$_{5b}$		-0.14151	
Q$_{6b}$		0.029184	
Q$_{7b}$		-0.20748	
Q$_{8b}$			
Q$_9$		0.14030	
Q$_{10}$	0.43250	0.32166	
Q$_{11}$	-0.0008887	0.21813	
Q$_{12a}$	0.61178	0.47400	
Q$_{13a}$	0	-0.27575	
Q$_{14a}$	0	0.23907	
Q$_{12b}$		-0.17322	
Q$_{13b}$		-0.12860	
Q$_{14b}$			

2.4.

Table XXI (Continued).

(C_3H_6)	t	t*	t**
Q_1	0.73364	0.33190	0.71975
Q_2	−0.070034	0.36235	0.23743
Q_3	−0.39361	0.51190	0.14991
Q_{5a}	1.03752	−0.23469	−0.50894
Q_{6a}	0.0072311	−0.42886	−0.33548
Q_{7a}	−0.56340	−0.43091	−0.15744
Q_{8a}	0.046764	−0.27393	−0.22755
Q_9			−0.31590
Q_{10}		0.30779	
Q_{11}		0.63343	
Q_{12a}		−0.24532	0.92142
Q_{13a}		−0.035176	−0.46968
Q_{14a}		−0.66915	0.93541

Cyclopropane-d_6, C_3D_6

(C_3D_6)	r	r*	d
Q_1	0.20779	0.23072	0
Q_2	0	0.20240	0.095878
Q_3	0	−0.10957	−0.26177
Q_4		0.13451	
Q_{5a}	0.42114	0.32629	0
Q_{6a}	0	−0.15492	0.24654
Q_{7a}	0	0.18014	0.10922
Q_{8a}	0	0.048381	−0.088298
Q_{5b}		0.068872	
Q_{6b}		0.068820	
Q_{7b}		−0.18461	
Q_{8b}		0.099248	
Q_9			
Q_{10}	0.32333	0.23155	
Q_{11}	0.0006008	0.15707	
Q_{12a}	0.45725	0.35427	
Q_{13a}	0	−0.23605	
Q_{14a}	0	0.16401	

2.4.

Table XXI (Continued).

Q_{12b}		−0.13068	
Q_{13b}		−0.095114	
Q_{14b}			

(C_3D_6)	t	t'	t''
Q_1	0.52789	0.23882	0.51789
Q_2	−0.20467	0.43518	0.30926
Q_3	−0.21565	0.095738	−0.061383
Q_{5a}	0.74655	−0.16887	−0.36621
Q_{6a}	0.036027	0.0080956	−0.0050511
Q_{7a}	−0.41891	−0.26074	−0.070710
Q_{8a}	−0.0004854	−0.39403	−0.30599
Q_9			−0.22346
Q_{10}		0.20435	
Q_{11}		0.45433	
Q_{12a}		−0.18335	0.68868
Q_{13a}		0.014066	−0.38241
Q_{14a}		−0.47636	0.056415

coordinates ($r = VS$), is given implicitly by equations
(64). Hence the K matrix ($r = KQ$) may be determined
according to equation (2.27), where the L matrix is known
(see Table XX). The coefficients of the K matrix are
given numerically in Table XXI.

Now the mean amplitudes of vibration are obtainable
according to the theory described in the present chapter
[see section 2.1, especially equations (2.16) and (2.22)].
The results for both cyclopropane and cyclopropane-d_6
at the temperatures 0 and 298 °K, are listed in Table
XXII.

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2.4.

Table XXII. Mean amplitudes of vibration in cyclopropane and cyclopropane-d_6.

Molecule	Distance	Mean amplitude in Å	
		$T = 0$	298 °K
C_3H_6	C–H	0.0750	0.0750
	C··H	0.1082	0.1090
	C–C	0.0510	0.0514
	H_1··H_1'	0.1180	0.1181
	H_2··H_3	0.1758	0.1783
	H_2··H_3'	0.1316	0.1320
C_3D_6	C–D	0.0643	0.0643
	C··D	0.0944	0.0964
	C–C	0.0506	0.0511
	D_1··D_1'	0.1007	0.1010
	D_2··D_3	0.1484	0.1552
	D_2··D_3'	0.1137	0.1148

3. ASSUMPTIONS OF SIMPLIFIED MOLECULAR MODELS IN THE CALCULATION OF MEAN AMPLITUDES OF VIBRATION

3.1. Introduction

In many cases the computations of mean amplitudes of vibration may be greatly facilitated by assuming simplified molecular models, and still valuable results obtained, if not a too great accuracy is claimed. In fact, such an approximate assumption has been made in one of the first computations of mean amplitudes of vibration, where dimethyldiacetylene was considered as a six-particle linear structure (5). Moreover, approximate calculations of the mean amplitudes of vibration for the benzene ring (35), as well as those for the allene skeleton (34), have been carried out by the present author, and compared with the more rigorous calculations (25), (27), (33) with encouraging results. Also some approximate calculations for cyclopropane (16) and normal-butane (37) have been reported.

For the estimation of the mean amplitude of vibration for a bonded atom pair containing hydrogen (C-H, N-H, P-H, etc.) it seems plausible to treat the problem as a two-particle structure, namely as a hydrogen atom attached to the rest of the molecule. Such a treatment is actually based on the assumption of a special kind of simplified molecular models, and has been applied for instance to C-H in dimethyldiacetylene (5), and to P-H in phosphine (16).

3.2.

3.2. Application to X-Y of the cyclopropane moleoular model.

The cyclopropane molecular model X_3Y_6 is considered. An approximate formula for the mean-square amplitude of vibration for the bonded X-Y (C-H or C-D) atom pair, is obtained as

$$u_{X-Y}^2 = (h/8\pi^2\nu)(\mu_R + \mu_Y) , \qquad (3.1)$$

if the simple two-particle model X_3Y_5-Y is adopted. Here μ_Y is the inverse mass of the Y atom, and μ_R that of the X_3Y_5 group. For ν in equation (1) a X-Y stretching frequency should be inserted. The temperature-dependent factor could be omitted in this case, since the frequency is assumed to have an extremely high value (as is the case with C-H and C-D stretching frequencies). Equation (1) has the same form as that for diatomic molecules. References are made to Table IV, and also equations (2.8) and (2.9).

The present method has been applied to the C-H and C-D mean amplitudes of vibration in C_3H_6 and C_3D_6, respectively. As a part of the approximation, it was assumed that the totally symmetrical C-H and C-D stretohing normal frequencies for cyclopropane and cyclopropane-d_6

Table XXIII. C-H and C-D mean amplitudes of vibration for cyclopropane and cyclopropane-d_6, regarded as two-particle structures.

Distance	Mean amplitude in Å
C-H	0.0720
C-D	0.0606

3.2.

could be applied to the present model. With the values
3301.3 cm^{-1} and 2375.4 cm^{-1}, respectively (see Table
XVII), the result given in Table XXIII was obtained.
The deviations from the more rigorously calculated
values (Table XXII) are -0.0030 Å and -0.0037 Å for
C-H and C-D, respectively.

It should be noted that the approximate mean ampli-
tude of vibration for C-H in cyclopropane previously
communicated ([18]), is based on another method of approxi-
mation, which is different from the present one. That
method is described elsewhere [see reference ([12])], and
has proved to be better than the two-particle method
applied here.

3.3. Application to the ring of the cyclopropane
molecular model

In this section the cyclopropane molecules will be
treated as regular trigonal X$_3$ structures (see Fig. 3),
where X = CH$_2$ or CD$_2$. According to Table IV, one has

$$u^2_{X-X} = (h/8\pi^2)\mu_X\left\{ \nu(A_1')^{-1} \coth[h\beta\nu(A_1')/2] + \nu_2(E')^{-1} \coth[h\beta\nu(E')/2] \right\}. \quad (3.2)$$

This formula is expected to give a reasonable approxima-
tion for the C-C mean-square amplitudes of vibration in
cyclopropane and cyclopropane-d$_6$, if the appropriate
C-C stretching normal frequencies are inserted. The
numerical values from Table XVII have been taken, viz.
$\nu(A_1')/c$ = 1188.0 cm^{-1}, $\nu(E')/c$ = 1050.6 cm^{-1} for C$_3$H$_6$,
and $\nu(A_1')/c$ = 956 cm^{-1}, $\nu(E')/c$ = 903.2 cm^{-1} for C$_3$D$_6$.

3.3.

Table XXIV. C–C mean amplitudes of vibration for the
cyclopropane ring, based on the adoptation of a regular
trigonal structure.

| Molecule | Distance | Mean amplitude in Å [a]) | |
		T = 0	298 °K
C_3H_6	C–C	0.0464 (–0.0046)	0.0467 (–0.0047)
C_3D_6	C–C	0.0476 (–0.0030)	0.0481 (–0.0030)

[a]) The deviations from the rigorous values (Table XXII) are
included in parentheses.

The computed mean amplitudes of vibration are found in
Table XXIV, together with the respective deviations
from the more rigorously calculated values (Table XXII).

The force constants may be introduces according
to equations (2.40), where $\lambda_1 = 4\pi^2\nu(A_1')^2$ and $\lambda_2 = 4\pi^2\nu(E')^2$ should be inserted. From equation (2.41) the
following simplified formula is obtained for T = 0, if
the interaction constant k' is omitted.

$$u_{X-X}^2 = 3^{-\frac{1}{2}}(1 + 2^{\frac{1}{2}})(h/4\pi)\mu_X^{\frac{1}{2}}k^{-\frac{1}{2}}. \qquad (3.3)$$

Following this procedure, the result for C_3H_6 is k =
5.3456 mdyne Å^{-1}, u = 0.0456 Å (T=0), and for C_3D_6:
k = 4.3821 mdyne Å^{-1}, u = 0.0464 Å (T=0).

In the previously cited paper [18] the same method
has been applied to the cyclopropane ring, but is based
on another assignment of the vibrational frequencies,
taken from Herzberg [64].

3.4.

3.4. Discussion

It may be realized from the examples treated in
the present chapter, together with additional experience,
that the problem of calculating mean amplitudes of vib-
ration often may be largely facilitated by assuming
simplified molecular models. The results, however, should
not be accepted without criticism, if some values of
great accuracy are required. But valuable information
may be obtained if only the orders of magnitude of the
mean amplitudes of vibration are desired, as often is
the case by electron-diffraction investigations. Further-
more, it would still be worthwhile to apply the method
of simplified molecular models to more complicated cases
as, for instance, the condenced aromatic rings. In such
cases it seems to be rather hopeless to carry out the
rigorous calculations.

4. SECULAR EQUATIONS INVOLVING MEAN-SQUARE AMPLITUDES OF VIBRATION, AND MEAN-SQUARE AMPLITUDE MATRICES *)

4.1. Theory

Introduction. Some features of the ordinary secular equation **) in the problem of harmonic vibrations of polyatomic molecules will be summarized as an introduction to this section. The secular equation may be written in the form given by equation (2.20), viz.

$$|GF - \lambda E| = 0 . \qquad (4.1)$$

As shown in section 2.1, the equation is deduced from the relations

$$\tilde{L}FL = \Lambda , \qquad \tilde{L}G^{-1}L = E , \qquad (4.2)$$

which also may be given in a modified form as

$$L\Lambda^{-1}\tilde{L} = F^{-1} , \qquad L\tilde{L} = G . \qquad (4.3)$$

Here F and G denote respectively the potential energy matrix and the inverse kinetic energy matrix, in terms of a set of internal coordinates which will be represented by S. E is the identity matrix, and Λ a diagonal matrix with the elements

---

*) For original publications, see (39),(40),(41),(29),(30),(31),(32).

**) See references (135),(132),(134),(53),(122).

4.1.

$$\lambda_k = 4\pi^2 \nu_k^2 \qquad (4.4)$$

[cf. equations (2.17),(2.18)]. The matrix **L** is given by the linear transformation

$$S = L Q, \qquad (4.5)$$

where **Q** represents the vibrational normal coordinates [cf. equation (2.10)].

The secular equation (1) makes it possible to establish relations between the force constants including the interaction terms, and the normal frequencies of a molecule. It should be emphasized that the number of normal frequencies in most cases is not sufficient for the complete determination of the harmonic force field. Therefore usually additional assumptions are made, e.g. simplifications of the force field, assumption of a Urey-Bradley field (124),(114),(115),(116), or applications of force constant values from related molecules. Furthermore, the normal frequencies from isotopically substituted molecules may be utilized for this purpose. Once the complete **F** matrix is established and with the knowledge of the **G** matrix and the normal frequencies, the **L** matrix of equation (5) is obtainable by means of the method of characteristic vectors.

Further secular equations. The following additional symbols will be applied.

$$\Sigma = S \tilde{S} , \qquad (4.6)$$

$$\Sigma_{11} = \overline{s_1^2} , \qquad \Sigma_{ij} = \overline{s_i s_j} . \qquad (4.7)$$

$$\Delta = Q \tilde{Q} , \qquad (4.8)$$

4.1.

$$\Delta_k = (h/8\pi^2\nu_k)\coth(h\beta\nu_k/2) \tag{4.9}$$

The elements on the main diagonal of the matrix Σ, viz. Σ_{ii}, are the respective mean-square amplitudes of vibration. The off-diagonal elements, viz. Σ_{ij} ($i \neq j$), will be referred to as the i n t e r a c t i o n   m e a n - s q u a r e   a m p l i t u d e s , and the matrix itself the m e a n - s q u a r e   a m p l i t u d e m a t r i x . The matrix of equation (8) is a diagonal matrix with the elements $\Delta_k = \overline{Q_k^2}$ given by (9) in conformity with equation (2.14). The relations

$$\widetilde{L}\,\Sigma^{-1}L = \Delta^{-1}\,, \qquad L\Delta\widetilde{L} = \Sigma \tag{4.10}$$

exist in addition to those of equations (2) and (3). The latter one of the equations (10) may be identified with equation (2.11). By means of equations (2) and (10), additional secular equations may be derived in a similar way, as outlined in section 2.1, and written in the forms

$$|\Sigma G^{-1} - \Delta E| = 0 \, , \tag{4.11}$$

$$|\Sigma F - \lambda\Delta E| = 0 \, . \tag{4.12}$$

According to equations (4) and (9), the characteristic values of the ΣF matrix are

$$\lambda_k\Delta_k = \tfrac{1}{2}h\nu_k\coth(h\beta\nu_k/2) \, . \tag{4.13}$$

Applications of the secular equations. In the following will be outlined some methods of calculation utilizing the reported secular equations. The normal frequencies and the G matrix elements are considered as

4.1.

known quantities.

(i) In the method developed by Morino et al.(97), equation (1) is applied (cf. chapter 2 and also the introduction above). The F matrix is established by means of the normal frequencies of the molecule and occasionally further information and additional assumptions. Consequently the L matrix is deducible, and the whole Σ matrix may be obtained from the latter one of equations (10).

(ii) In an analogous way, equation (11) may be applied to establish relations connecting the normal frequencies and the mean-square amplitudes of vibration, including interaction terms. Here again the number of normal frequencies is usually not sufficient for the complete determination of the mean-square amplitude matrix, and the method makes it possible to introduce assumptions about the matrix elements w i t h o u t s p e c i f y i n g the f o r c e f i e l d . If the complete Σ matrix could be established in this way, it would be possible to determine the L matrix by the method of characteristic vectors applied to the ΣG^{-1} matrix. In consequence, the F matrix, or rather its inverse, could be obtained from the first one of equations (3).

(iii) By means of equation (12), relations containing the elements from both of the matrices Σ and F are obtainable. These relations will be useful in combination with the relations obtained from (1) and (11) if it is desirable to apply some information about the Σ matrix elements for determination of the elements of the F matrix, and vice versa. Accordingly,

4.1.

such calculations may be performed without determination of the **L** matrix.

If the coordinates **S** are chosen as a set of symmetry coordinates, both of the new secular equations will factorize in precisely the same manner as the ordinary secular equation (1).

The symmetry coordinates may be formed as an orthogonal transformation of a set of internal coordinates, denoted by **q** . Hence the relations of the form (2.21), where **R** is the transformation matrix, may be used for detecting the connection between various quantities in terms of the two coordinate sets. To show an example, it is found

$$P = \tilde{R} \Sigma R \ , \qquad \Sigma = R P \tilde{R} \ , \qquad (4.14)$$

where the symbol **P** is defined by

$$P = \overline{q \tilde{q}} \ . \qquad (4.15)$$

In practice, the mean amplitudes of vibration given by equation (1.1), where R is the distance between a pair of bonded or non-bonded atoms, are the most important ones. In consequence, it will often be convenient to let **q** be composed of merely interatomic distance deviations, i.e. a set of central force coordinates.

For practical computations some further transformations must be considered. If **r** and **K** have the same meanings as previously [see equation (2.23)], the symbol **P** will for a moment be used as given by

$$P = \overline{r \tilde{r}} = K \Delta \tilde{K} \ . \qquad (4.16)$$

4.1.

For this mean-square amplitude matrix it is found

$$P = V\Sigma\tilde{V}. \tag{4.17}$$

The matrix V appearing in this equation is defined by equation (2.25), and may be computed according to (2.26).

    Isotope rules. The ordinary product rule[*] for isotopically substituted molecules as derived from equation (1) may be written in the form [133], [134]

$$\prod_i (\nu_i/\nu_i^*) = |G|^{\frac{1}{2}}/|G^*|^{\frac{1}{2}}, \tag{4.18}$$

where the quantities of the isotopically substituted molecule are identified by an asterisk. Using the analogous notation, one obtains from equation (12)

$$|\Sigma|/|\Sigma^*| = \prod_i \frac{\nu_i \coth(h\beta\nu_i/2)}{\nu_i^* \coth(h\beta\nu_i^*/2)}. \tag{4.19}$$

If the mean-square amplitudes at the absolute zero are considered, and the notation Σ_o is used for the corresponding mean-square amplitude matrix, one obtains

$$|\Sigma_o|/|\Sigma_o^*| = \prod_i (\nu_i/\nu_i^*) = |G|^{\frac{1}{2}}/|G^*|^{\frac{1}{2}}. \tag{4.20}$$

4.2. Treatment of simple molecular models.

    Here the simple molecular models which were treated in section 2.2 will be considered. In such cases the secular equations factorize into linear equations, and

---

*) The Teller—Redlich product rule; see reference (107).

4.2.

simple relations are obtained.

Formulae involving mean-square amplitudes of vibration. As an example, the linear symmetrical XY_2 molecule model will be treated in some detail. The mean-square amplitude matrices, in terms of the bond length displacements (see Fig. 2) and in terms of the symmetry coordinates of equation (2.30), may be written in the following way.

$$
\Sigma: \quad
\begin{array}{c} r_1 \\ r_2 \end{array}
\begin{array}{cc} r_1 & r_2 \\ \left[\begin{array}{cc} \sigma & \sigma' \\ \sigma' & \sigma \end{array} \right] \end{array}
\qquad
\begin{array}{c} S_1 \\ S_3 \end{array}
\begin{array}{cc} S_1 & S_3 \\ \left[\begin{array}{cc} \sigma+\sigma' & 0 \\ 0 & \sigma-\sigma' \end{array} \right] \end{array}
$$

The secular equation (11) gives straightforwadly

$$
\Delta_1 = (\sigma+\sigma')\,\mu_Y^{-1} \ , \qquad \Delta_3 = (\sigma-\sigma')(2\mu_X+\mu_Y)^{-1} \ , \qquad (4.21)
$$

which may be solved for the mean-square amplitude quantities and yields the result

$$
\sigma = \tfrac{1}{2}\big[\,\Delta_1\mu_Y + \Delta_3(2\mu_X+\mu_Y)\big] \ ,
$$
$$
\sigma' = \tfrac{1}{2}\big[\,\Delta_1\mu_Y - \Delta_3(2\mu_X+\mu_Y)\big] \ . \qquad (4.22)
$$

The Δ-values are given acoording to equation (9). From the secular equation (12), the following relations between the force constants defined by equation (2.31), and the mean-square amplitude quantities, have been deduced.

$$
\lambda_1\Delta_1 = (\sigma+\sigma')(k+k') \ , \qquad \lambda_3\Delta_3 = (\sigma-\sigma')(k-k'). \qquad (4.23)
$$

The equations have been solved for the mean-square

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amplitude quantities with the result

$$\sigma = \tfrac{1}{2}\left[\lambda_1 \Delta_1 (k+k')^{-1} + \lambda_3 \Delta_3 (k-k')^{-1}\right],$$

$$\sigma' = \tfrac{1}{2}\left[\lambda_1 \Delta_1 (k+k')^{-1} - \lambda_3 \Delta_3 (k-k')^{-1}\right].$$

(4.24)

Similar expressions are obtained for the force constants, viz.

$$k = \tfrac{1}{2}\left[\lambda_1 \Delta_1 (\sigma+\sigma')^{-1} + \lambda_3 \Delta_3 (\sigma-\sigma')^{-1}\right],$$

$$k' = \tfrac{1}{2}\left[\lambda_1 \Delta_1 (\sigma+\sigma')^{-1} - \lambda_3 \Delta_3 (\sigma-\sigma')^{-1}\right].$$

(4.25)

A new mean-square amplitude matrix may be constructed if the interatomic distance deviations given by equations (2.35) and (2.36) are introduced. This matrix is given by

$$
\begin{array}{c c}
& \begin{array}{c c} r_{X-Y} & r_{Y\cdots Y} \end{array} \\
\begin{array}{c} r_{X-Y} \\ r_{Y\cdots Y} \end{array} &
\left[
\begin{array}{c c}
\sigma & \sigma+\sigma' \\
 & 2(\sigma+\sigma')
\end{array}
\right]
\end{array}
$$

The diagonal elements of the matrix represent the mean-square amplitudes of vibration for the bonded and non-bonded distances, respectively, i.e. $u_{X-Y}^2 = \sigma$, $u_{Y\cdots Y}^2 = 2(\sigma+\sigma')$. If these quantities are computed by means of equations (22), expressions identical with those given in Table IV are obtained, provided that ν_1 and ν_3 are inserted in accordance with equation (9). Alternatively, the equations (24) may be applied for

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Table XXV. Mean-square amplitudes of vibration of simple molecular models.II.[*])

Molecule	Distance	Mean-square amplitude of vibration
Diatomic	X–Y	$\frac{1}{2}h\nu k^{-1} \coth(h\beta\nu/2)$
Linear symm. XY_2	X–Y	$\frac{1}{4}[h\nu_1(k+k')^{-1}\coth(h\beta\nu_1/2)$
		$+ h\nu_3(k-k')^{-1}\coth(h\beta\nu_3/2)]$
	Y··Y	$h\nu_1(k+k')^{-1}\coth(h\beta\nu_1/2)$
Regular trig. X_3	X–X	$\frac{1}{3}[\frac{1}{2}h\nu_1(k+2k')^{-1}\coth(h\beta\nu_1/2)$
		$+ h\nu_2(k-k')^{-1}\coth(h\beta\nu_2/2)]$
Plane square X_4	X–X	$\frac{1}{4}\{\frac{1}{2}h\nu_1(k+2k'+k'')^{-1}\coth(h\beta\nu_1/2)$
		$+ \frac{1}{2}h\nu_2(k-2k'+k'')^{-1}\coth(h\beta\nu_2/2)$
		$+ \frac{1}{2}h\nu_6[k-k''+2(f-f'')-4(g-g')]^{-1}\coth(h\beta\nu_6/2)\}$
	X··X	$\frac{1}{4}[h\nu_1(k+2k'+k'')^{-1}\coth(h\beta\nu_1/2)$
		$+ \frac{1}{4}h\nu_3(f-2f'+f'')^{-1}\coth(h\beta\nu_3/2)]$
Tetra-hedral X_4	X–X	$\frac{1}{3}[\frac{1}{6}h\nu_1(k+4k'+k'')^{-1}\coth(h\beta\nu_1/2)$
		$+ \frac{1}{3}h\nu_2(k-2k'+k'')^{-1}\coth(h\beta\nu_2/2)$
		$+ \frac{1}{2}h\nu_3(k-k'')^{-1}\coth(h\beta\nu_3/2)]$

*) For I ; see Table IV.

4.2.

computing the mean-square amplitudes of vibration under
consideration. The expressions deduced after inserting
ν_1 and ν_3 in accordance with equation (13) are included
in Table **XXV** . The force constants enter into these
expressions, but, in contrast to the equations (2.37)
and (2.38) the atomic masses do not appear in the
expressions of Table **XXV** . This table contains the
corresponding formulae for all the molecular models
treated in section 2.2 (cf. Table IV).

Numerical examples. It seems suitable to include
some numerical results in this section, to show the
orders of magnitude of the introduced quantities. The
following molecules have been chosen as examples: (a)
The diatomic molecules O_2, S_2 and Se_2, (b) carbon
dioxide, disulphide and diselenide of the linear symmetri-
cal XY_2 type, and (c) P_4, being a tetrahedral molecule.
The spectroscopic data used in the calculations are
given in Table **XXVI** , and the numerical results in
Table **XXVII.**

The force constants k, k' and k", appearing in
Table **XXVII**, are defined in section 2.2. For the meaning
of the symbols σ and σ' in the case of linear symmetrical
XY_2 molecules, the preceeding paragraph should be con-
sulted. In the case of tetrahedral X_4 molecules, the
symbols adopted for the mean-square amplitude quantities
are given by

$$\sigma = \overline{r_1^2} , \qquad \sigma' = \overline{r_1 r_2} , \qquad \sigma" = \overline{r_1 r_4} , \qquad (4.26)$$

where the notation of Fig. 5 is used.

For the respective mean amplitudes of vibration
of the various interatomic distances of the molecules

4.2.

Table XXVI. Normal frequencies and related quantities of
specific molecules.

Molecule	Species	ω [a])	λ/N [c])	$N\Delta$ [d])	
				T=0	298°K
$^{16}O_2$		1580.361	1.4709	0.010670	0.010680
$^{32}S_2$		725.68	0.31014	0.023237	0.024681
$^{80}Se_2$		391.77	0.09039	0.043042	0.058351
$^{12}CO_2$	A_{1g}	1354.42[b])	1.0804	0.012450	0.012486
	A_{2u}	2396.40	3.3821	0.007037	0.007037
$^{13}CO_2$	A_{1g}	1354.42[b])	1.0804	0.012450	0.012486
	A_{2u}	2328.20	3.1923	0.007243	0.007243
$^{14}CO_2$	A_{1g}	1354.42[b])	1.0804	0.012450	0.012486
	A_{2u}	2268.33	3.0302	0.007434	0.007434
CS_2	A_{1g}	671.4	0.26548	0.025116	0.027163
(gas)	A_{2u}	1551.92	1.4184	0.010866	0.010878
CSe_2	A_{1g}	371	0.08106	0.045452	0.063663
(gas)	A_{2u}	1310	1.0107	0.012872	0.012919
P_4	A_1	604	0.21485	0.027918	0.031119
	E	381	0.03549	0.044259	0.060999
	F_2	506	0.15079	0.033325	0.039677

[a]) In cm^{-1} units; all values corrected for anharmonicity. Data
for the diatomic molecules are quoted from Herzberg ([44]), for
the triatomic molecules from Wentink ([159]), and for phosphorus
from Pistorius ([99]). The cited publications include references
to the original sources.

[b]) Corrected for Fermi resonance.

[c]) In mdyne $Å^{-1}(Amu)^{-1}$. N is Avogadro's number. [d]) In $Å^2 Amu$.

4.2.

Table XXVII. Summary of calculations for the
molecules of Table XXVI.

Molecule	Species	Force constant[a]	Mean-square amplitude[b]	
			T=0	298°K
$^{12}CO_2$	A_{1g}	17.2859	0.0007781	0.0007804
	A_{2u}	14.7616	0.0016122	0.0016122
$^{13}CO_2$	A_{1g}	17.2859	0.0007781	0.0007804
	A_{2u}	14.7617	0.0015663	0.0015663
$^{14}CO_2$	A_{1g}	17.2859	0.0007781	0.0007804
	A_{2u}	14.7616	0.0015260	0.0015261
CS_2	A_{1g}	8.5128	0.0007832	0.0008471
	A_{2u}	7.1741	0.0021483	0.0021507
CSe_2	A_{1g}	6.4006	0.0005756	0.0008063
	A_{2u}	5.6401	0.0023066	0.0023149
P_4	A_1	1.6643	0.0036042	0.0040174
	E	2.6488	0.0014284	0.0019687
	F_2	2.3360	0.0021511	0.0025611

Molecule	Force constant[a]		Mean-square amplitude[b]	
			T=0	298°K
$^{16}O_2$	k	23.5341	σ	0.0013338	0.0013351
$^{32}S_2$	k	9.9185	σ	0.0014532	0.0015435
$^{80}Se_2$	k	7.2313	σ	0.0010761	0.0014588
$^{12}CO_2$	k	16.0238	σ	0.0011952	0.0011963
	k'	1.2621	σ'	−0.0004170	−0.0004159
$^{13}CO_2$	k	16.0238	σ	0.0011722	0.0011734
	k'	1.2621	σ'	−0.0003941	−0.0003930

4.2.

Table XXVII (Continued).

$^{14}CO_2$	k	16.0238	σ	0.0011521	0.0011532
	k'	1.2621	σ'	−0.0003740	−0.0003728
CS_2	k	7.8434	σ	0.0014658	0.0014989
	k'	0.66936	σ'	−0.0006825	−0.0006518
CSe_2	k	6.0204	σ	0.0014411	0.0015606
	k'	0.38024	σ'	−0.0008655	−0.0007543
P_4	k	2.3283	σ	0.0021524	0.0026064
	k'	−0.16410	σ'	0.00036263	0.00034145
	k''	−0.00769	σ''	0.00000128	0.00004526

a) In mdyne Å^{-1} units. b) In Å^2 units.

here considered, reference is made to Table LI.

4.3. Valence force mean-square amplitudes and central force mean-square amplitudes approximations

It has been pointed out in the first section of this chapter that the number of normal frequencies of a polyatomic molecule usually is not sufficient for the complete determination of the vibrational constants. To eliminate this difficulty, usually certain approxi-

4.3.

mationa are introduced. When the ordinary secular
equation is applied, it is convenient to introduce
some assumptions about the force constants. If the
F matrix in terms of a set of valence force coordi-
nates or central force coordinates is assumed to have
a completely diagonal form, the approximations are
referred to as the simple valence force field and
central force field, respectively [see, e.g. (⁴⁴) and
(⁴⁵)]. Modified valence force fields or central force
fields are obtained if only some of the off-diagonal
elements of the respective **F** matrices are assumed to
be negligible.

An analogous procedure may be followed if the
secular equation (11) is applied for determining the
vibrational constants of a polyatomic molecule. If
the **Σ** matrix in terms of a set of valence force
coordinates is assumed to be of the diagonal form,
the approximation will be referred to as the
v a l e n c e   f o r c e   m e a n - s q u a r e
a m p l i t u d e s   approximation, and in terms of
a set of central force coordinates the   c e n t r a l
f o r c e   m e a n - s q u a r e   a m p l i t u d e s.
The modified valence force mean-square amplitudes and
central force mean-square amplitudes approximations are
obtained if only some of the respective **Σ** matrix off-
diagonal elements are assumed to be negligible.

It should be pointed out that the certain
assumptions about the elements of the **Σ** matrix lead to
different approximations, depending on the chosen
temperature.

4.4.

4.4. Treatment of bent symmetrical XY_2 molecules

The study of bent symmetrical XY_2 molecules has been the subject of many publications [see, e.g., (45), (113), (56), (40), (81), (116), (30)]. In the present section, some of the theoretical results for this type of molecules will be summarized and supplied with the study of the mean-square amplitude matrix. Numerical calculations for nitrogen dioxide will be reported.

Molecular symmetry. The bent symmetrical XY_2 molecular model (Fig. 8) belongs to the symmetry group C_{2v}. The normal modes of vibration are distributed among the various symmetrical species according to

$$\Gamma(Q) = 2A_1 + B_1 . \tag{4.27}$$

The following symmetry coordinates have been formed as normalized linear combinations of the valence force coordinates given by Fig. 8.

Symm. species A_1:
$$\begin{cases} S_1 = 2^{-\frac{1}{2}}(r_1 + r_2) , \\ S_2 = R\alpha , \end{cases}$$
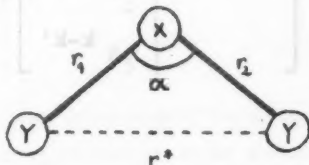
Fig. 8. Notation used for the bent symmetrical XY_2 molecular model (C_{2v}). The symbols denote the deviations from the equilibrium values. The equilibrium length of the X–Y bond is denoted by R, and the YXY angle is 2A.

4.4.

Symm.species B_1: $\qquad$ $S_3 = 2^{-\frac{1}{2}}(r_1-r_2)$. $\qquad$ (4.28)

It should be noticed that the angle displacement coordinate α is multiplied by R, designating the equilibrium X–Y distance.

$\qquad$ Energy matrices and mean-square amplitude matrices. The harmonic potential energy function (V) contains four different force constants and is given in terms of the valence force coordinates by

$$2V = k(r_1^2+r_2^2) + 2k'r_1r_2 + fR^2\alpha^2 + 2g(r_1+r_2)\alpha. \qquad (4.29)$$

Hence k and k' may be interpreted as the bond stretching and the bond-bond interaction constants, respectively, f as the valence angle bending, and g as the bond-angle interaction constant. The F and G matrices in terms of the valence force coordinates, as well as the chosen symmetry coordinates are given in the following [see, e.g. (94) and (96)].

	r_1	r_2	$R\alpha$		S_1	S_2	S_3
r_1	k	k'	g	S_1	k+k'	$2^{\frac{1}{2}}g$	0
F: r_2		k	g	S_2	f		0
$R\alpha$			f	S_3			k-k'

4.4.

$$
\mathbf{G}: \quad
\begin{array}{c}
\\
r_1 \\
r_2 \\
Ra
\end{array}
\overset{\begin{array}{ccc} r_1 & r_2 & Ra \end{array}}{
\begin{bmatrix}
\mu_X + \mu_Y & \mu_X \cos 2A & -\mu_X \sin 2A \\
 & \mu_X + \mu_Y & -\mu_X \sin 2A \\
 & & 2(2\mu_X \sin^2 A + \mu_Y)
\end{bmatrix}}
$$

$$
\mathbf{G}: \quad
\begin{array}{c}
\\
s_1 \\
s_2 \\
s_3
\end{array}
\overset{\begin{array}{ccc} s_1 & s_2 & s_3 \end{array}}{
\begin{bmatrix}
2\mu_X \cos^2 A + \mu_Y & -2^{\frac{1}{2}}\mu_X \sin 2A & 0 \\
 & 2(2\mu_X \sin^2 A + \mu_Y) & 0 \\
 & & 2\mu_X \sin^2 A + \mu_Y
\end{bmatrix}}
$$

μ_X and μ_Y denote the inverse masses of the X and Y atoms, respectively, and the equilibrium value of the YXY angle is 2A. For the inverse of the symmetrized F and G matrices it is found:

$$
\mathbf{F}^{-1}: \quad
\begin{array}{c}
\\
s_1 \\
s_2 \\
s_3
\end{array}
\overset{\begin{array}{ccc} s_1 & s_2 & s_3 \end{array}}{
\begin{bmatrix}
\Phi/(\kappa_1 \phi - \Gamma^2) & -\Gamma/(\kappa_1 \phi - \Gamma^2) & 0 \\
 & \kappa_1/(\kappa_1 \phi - \Gamma^2) & 0 \\
 & & 1/\kappa_3
\end{bmatrix}}
$$

The various mean-square amplitudes of vibration and interaction mean-square amplitudes here appearing may be specified as follows.

4.4.

$$
G^{-1}: \begin{array}{c} \\ s_1 \\ s_2 \\ s_3 \end{array}
\begin{array}{c}
 \quad s_1 \qquad\qquad s_2 \qquad\qquad s_3
\end{array}
\left[
\begin{array}{ccc}
\dfrac{2\mu_X \sin^2 A + \mu_Y}{(2\mu_X + \mu_Y)\,\mu_Y} & \dfrac{2^{\frac{1}{2}}\mu_X \sin 2A}{2(2\mu_X + \mu_Y)\mu_Y} & 0 \\[3mm]
& \dfrac{2\mu_X \cos^2 A + \mu_Y}{2(2\mu_X + \mu_Y)\mu_Y} & 0 \\[3mm]
& & \dfrac{1}{2\mu_X \sin^2 A + \mu_Y}
\end{array}
\right]
$$

In the F^{-1} matrix the elements have been expressed in terms of the force constants of the symmetrized potential energy matrix, i.e.

$$ \kappa_1 = k+k', \quad \phi = f, \quad \Gamma = 2^{\frac{1}{2}}g, \quad \kappa_3 = k-k'. \qquad (4.30) $$

The mean-square amplitude matrices in terms of the two coordinate sets are given by:

$$
\Sigma:
\begin{array}{c} \\ r_1 \\ r_2 \\ R\alpha \end{array}
\begin{array}{c} r_1 \quad r_2 \quad R\alpha \end{array}
\left[
\begin{array}{ccc}
\sigma & \sigma' & \rho \\
 & \sigma & \rho \\
 & & \tau
\end{array}
\right]
\qquad
\begin{array}{c} \\ s_1 \\ s_2 \\ s_3 \end{array}
\begin{array}{c} s_1 \quad s_2 \quad s_3 \end{array}
\left[
\begin{array}{ccc}
\sigma+\sigma' & 2^{\frac{1}{2}}\rho & 0 \\
 & \tau & 0 \\
 & & \sigma-\sigma'
\end{array}
\right]
$$

The various mean-square amplitudes of vibration and interaction mean-square amplitudes here appearing, may be specified as follows.

4.4.

$$\sigma = \overline{r_1^2} = \overline{r_2^2} \ , \qquad \sigma' = \overline{r_1 r_2} \ , \qquad \tau = R^2 \, \overline{\alpha^2} \ ,$$

$$\rho = R \, \overline{r_1 \alpha} = R \, \overline{r_2 \alpha} \ .$$
(4.31)

The mean-square amplitude quantities of the symmetrized Σ matrix will lately be identified, similarly to the force constants of equation (30), by the symbols

$$\Sigma_1 = \sigma + \sigma' , \quad \Sigma_2 = \tau , \quad \Sigma_{12} = 2^{\frac{1}{2}} \rho , \quad \Sigma_3 = \sigma - \sigma' . \qquad (4.32)$$

Normal frequencies. The ordinary secular equation yields the following expressions for the normal frequencies ($\lambda = 4\pi^2 \nu^2$).

$$\lambda_1 + \lambda_2 = K_1 (2\mu_X \cos^2 A + \mu_Y) + 2\phi(2\mu_X \sin^2 A + \mu_Y)$$

$$- 8^{\frac{1}{2}} \Gamma \mu_X \sin 2A ,$$
(4.33)

$$\lambda_1 \lambda_2 = 2(K_1 \phi - \Gamma^2)(2\mu_X + \mu_Y)\mu_Y ,$$

$$\lambda_3 = K_3 (2\mu_X \sin^2 A + \mu_Y) .$$

Similar relations are obtained from the secular equation (11) and given below $[\Delta = (h/8\pi^2 \nu)\coth(h\beta\nu/2)]$.

$$\Delta_1 + \Delta_2 = [\, \Sigma_1 (2\mu_X \sin^2 A + \mu_Y) \ + \tfrac{1}{2} \Sigma_2 (2\mu_X \cos^2 A + \mu_Y)$$

$$+ 2^{\frac{1}{2}} \Sigma_{12} \mu_X \sin 2A](2\mu_X + \mu_Y)^{-1} \mu_Y^{-1} ,$$
(4.34)

$$\Delta_1 \Delta_2 = \tfrac{1}{2} (\Sigma_1 \Sigma_2 - \Sigma_{12}^2)(2\mu_X + \mu_Y)^{-1} \mu_Y^{-1} ,$$

$$\Delta_3 = \Sigma_3 (2\mu_X \sin^2 A + \mu_Y)^{-1} .$$

4.4.

The secular equation (12) yields the following relations, involving both the force constants and the mean-square amplitude quantities.

$$\lambda_1 \Delta_1 + \lambda_2 \Delta_2 = K_1 \Sigma_1 + \phi \Sigma_2 + 2\Gamma \Sigma_{12} ,$$

$$\lambda_1 \lambda_2 \Delta_1 \Delta_2 = (K_1 \phi - \Gamma^2)(\Sigma_1 \Sigma_2 - \Sigma_{12}^2), \quad (4.35)$$

$$\lambda_3 \Delta_3 = K_3 \Sigma_3 .$$

<u>Interatomic distance deviations.</u> There are two types of interatomic distances in the considered case, the appropriate distance deviations being represented by

$$r = r_1 , \qquad r^* = (r_1 + r_2)\sin A + R a \cos A . \quad (4.36)$$

In terms of the symmetry coordinates one has

$$r = 2^{-\frac{1}{2}}(S_1 + S_3) , \quad r^* = 2^{\frac{1}{2}}S_1 \sin A + S_2 \cos A . \quad (4.37)$$

A new mean-square amplitude matrix may be constructed as:

$$
\begin{array}{cc}
 & rr^* \\
\begin{array}{c} r \\ r^* \end{array} &
\left[
\begin{array}{cc}
\sigma & \sigma'^* \\
\sigma & \sigma^*
\end{array}
\right]
\end{array}
$$

For the elements of this matrix it is found

$$\sigma = \overline{r^2} , \quad \sigma'^* = \overline{rr^*} = (\sigma + \sigma')\sin A + \varrho \cos A ,$$

$$\sigma^* = \overline{(r^*)^2} = 2(\sigma + \sigma')\sin^2 A + \tau \cos^2 A + 2\varrho \sin 2A . \quad (4.38)$$

4.4.

Calculation of force constants for nitrogen

dioxide. The three frequencies of a specific bent symmetrical XY_2 molecule, say $^{14}NO_2$, are not sufficient for the complete determination of the harmonic force field. In the present case the frequency 1665.5 cm^{-1} (see Table XXVIII) gives the value $K_3 =$ 8.8927 mdyne $Å^{-1}$ without ambiguity for the force constant of the species B_1. The force constants of the species A_1, viz. K_1, ϕ and Γ are going to be discussed in the following. To obtain r e a l values of the force constants consistent with a set of normal frequencies, only a limited range for each

Table XXVIII. Experimental vibrational frequencies
of nitrogen dioxide molecules.

Species	No.	Normal frequencies (cm^{-1}) [a]	
		$^{14}NO_2$	$^{15}NO_2$
A_1	1	1357.8 [b]	1343.3 [b]
	2	756.8	747.1
B_1	3	1665.5	1628.6

[a]) From reference ([²]); all values corrected for anharmonicity.
The frequencies of $^{15}NO_2$ were revised to fit accurately
the product rule with the physical constants here applied,
the discrepancies from the values in the cited paper being
insignificant.

[b]) Based on estimated fundamentals from vibrational analysis.

4.4.
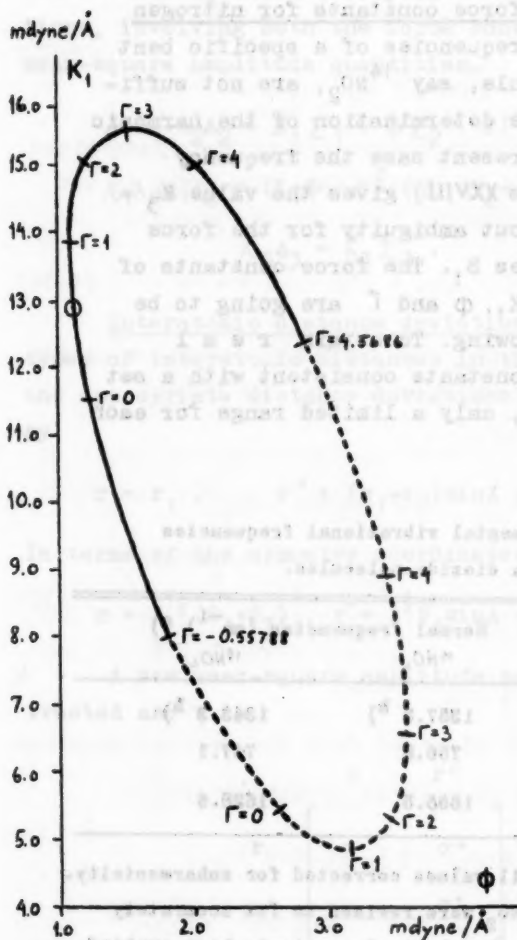
Fig. 9. Values of force constants for NO_2, compatible with $\omega_1 = 1357.8$ and $\omega_2 = 756.8$ cm^{-1}. $\odot$ indicates the best calculated values (see the text).

of the force constants is allowed. With the normal frequencies of $^{14}NO_2$ given in Table XXVIII, it is found from equation (33) for the interaction constant Γ in mdyne A^{-1} units

$$-0.55788 \leq \Gamma \leq 4.5686.$$

Several values of Γ within this range have been chosen, and the remaining force constants, viz. K_1 and Φ have been calculated. All the possible real values of the force constants have been represented graphically by an ellipse, shown in Fig. 9, this being a usual practice [see, e.g. (55), (56), (121), (51), (52), (113) (89), (118)]. The

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4.4.

stippled curve of Fig. 9 represents one set of the alter-
native solutions for the force constants, arising from
the quadratic secular equation.

Calculation of mean-square amplitude matrix
elements for nitrogen dioxide. The secular equation
(11) makes it possible to follow an analogue procedure
as shown in the preceding paragraph, in computing the
mean-square amplitude quantities. The magnitude of
1665.5 cm^{-1} for the normal frequency of species B_1 of
$^{14}NO_2$ yields the value $\Sigma_3 = 0.0018612$ $Å^2$ for the
corresponding mean-square amplitude matrix element at
298 ^{o}K. To obtain real values of the elements Σ_1 and
Σ_2 consistent with the normal frequencies of $^{14}NO_2$
given in Table XXVIII, the following restriction is
found from equations (34) for Σ_{12} at 298°K in $Å^2$ units.

$$-0.0022668 \leq \Sigma_{12} \leq -0.0003311 .$$

The graphical representation of all the possible real
values of the mean-square amplitude matrix elements of
the species A_1 and at the temperature 298 ^{o}K, is shown
in Fig. 10. One of the two simultaneous solutions for
each value of Σ_{12} is indicated by a stippled curve in
the figure.

In addition, also the possible real values of
the mean-square amplitude matrix elements defined in
equations (38) have been studied, and are plotted in
Fig. 11.

Further calculations for nitrogen dioxide. By
utilizing the normal frequencies of $^{15}NO_2$ in addition
to those of $^{14}NO_2$ (see Table XXVIII), the detection of

4.4.
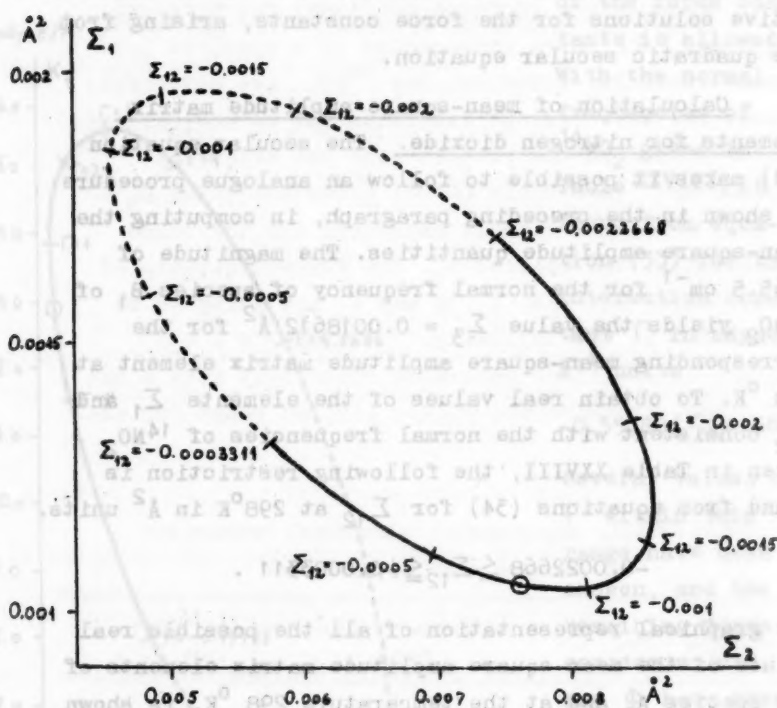
Fig.10. Values of mean-square amplitude matrix elements at 298 °K for $^{14}NO_2$, compatible with ω_1 = 1357.8 and ω_2 = 756.8 cm^{-1}. ⊙ indicates the best calculated values (see the text).

the complete sets of harmonic vibrational constants
is possible. The calculated force constants in terms
of the symmetry coordinates [see equations (30)], as

4.4.
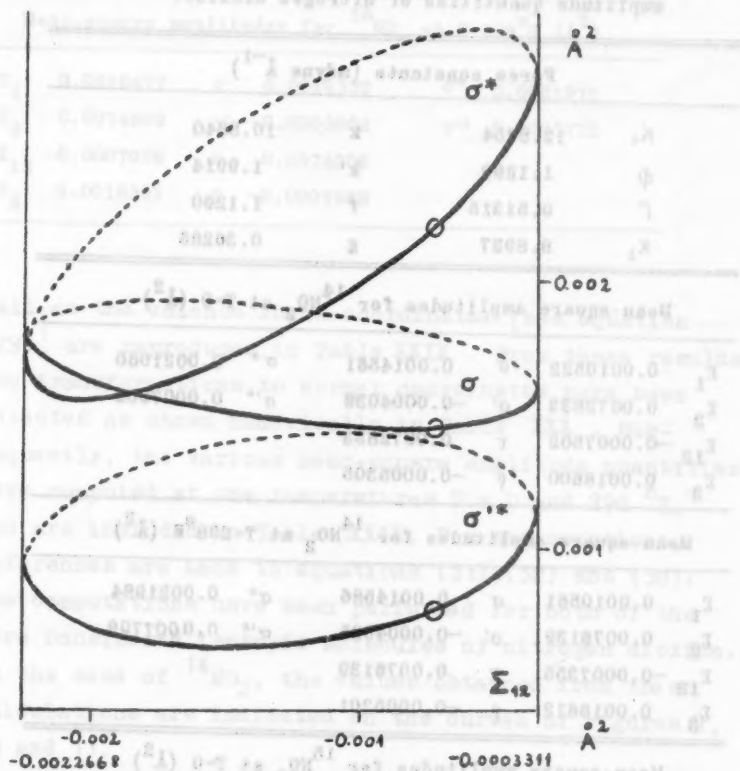
Fig. 11. Mean-square amplitude quantities at 298 $^\circ$K for $^{14}NO_2$, compatible with $\omega_1 = 1357.8$ and $\omega_2 = 756.8$ cm^{-1}. The best calculated values are indicated by $\odot$ (see the text).

4.4.

Table **XXIX**. Calculated force constants and mean-square
amplitude quantities of nitrogen dioxide.

Force constants (ndyne Å^{-1})			
K_4	12.8754	k	10.8840
ϕ	1.1290	k'	1.9914
Γ	0.51315	f	1.1290
K_3	8.8927	g	0.36285

Mean-square amplitudes for $^{14}NO_2$ at T=0 (Å^2)					
Σ_1	0.0010522	σ	0.0014561	σ^*	0.0021060
Σ_2	0.0072833	σ'	−0.0004039	σ'^*	0.0007632
Σ_{12}	−0.0007502	τ	0.0072833		
Σ_3	0.0018600	ρ	−0.0005305		

Mean-square amplitudes for $^{14}NO_2$ at T=298°K (Å^2)					
Σ_1	0.0010561	σ	0.0014586	σ^*	0.0021984
Σ_2	0.0076139	σ'	−0.0004025	σ'^*	0.0007709
Σ_{12}	−0.0007355	τ	0.0076139		
Σ_3	0.0018612	ρ	−0.0005201		

Mean-square amplitudes for $^{15}NO_2$ at T=0 (Å^2)					
Σ_1	0.0010438	σ	0.0014312	σ^*	0.0021249
Σ_2	0.0071348	σ'	−0.0003875	σ'^*	0.0007649
Σ_{12}	−0.0007160	τ	0.0071348		
Σ_3	0.0018187	ρ	−0.0005063		

4.4.

Table XXIX (Continued).

Mean-square amplitudes for $^{15}NO_2$ at T=298°K (Å^2)

Σ_1	0.0010477	σ	0.0014339	σ^s	0.0021975
Σ_2	0.0074809	σ'	−0.0003862	σ'^s	0.0007722
Σ_{12}	−0.0007026	τ	0.0074809		
Σ_3	0.0018201	ρ	−0.0004968		

well as the valence force coordinates [see equation (29)] are reproduced in Table XXIX . From these results the transformations to normal coordinates have been detected as shown numerically in Table XXX . Subsequently, the various mean-square amplitude quantities were computed at the temperatures T = 0 and 298 °K, and are included in Table XXIX. For the notations, references are made to equations (31),(32) and (38). The computations have been performed for both of the here considered isotopic molecules of nitrogen dioxide. In the case of $^{14}NO_2$, the values obtained from these calculations are indicated on the curves of Figures 9, 10 and 11.

The mean amplitudes of vibration for the bonded and non-bonded distances are given by $u_{X-Y} = \sigma^{\frac{1}{2}}$ and $u_{Y \cdot \cdot Y} = (\sigma^s)^{\frac{1}{2}}$, the numerical values of them being shown in Table XXXI.

Throughout the numerical calculations of this section, the value of 2A = 134°15′ (21),(8) has been applied for the equilibrium magnitude of the inter-bond angle in nitrogen dioxide.

4.4.

Table XXX. Coefficients of transformations involving
normal coordinates for $^{14}NO_2$ and $^{15}NO_2$ in $(Awu)^{-\frac{1}{2}}$ units.

$^{14}NO_2$	Q_1	Q_2	Q_3
S_1	0.28855	0.028558	...
S_2	−0.30261	0.52520	...
S_3	...	...	0.42861
r	0.20403	0.020194	0.30307
r^*	0.25834	0.24137	...

$^{15}NO_2$	Q_1	Q_2	Q_3
S_1	0.28637	0.025168	...
S_2	−0.28159	0.52154	...
S_3	...	...	0.41910
r	−0.20249	0.017796	0.29635
r^*	0.26368	0.23553	...

Isotope rules for $^{14}NO_2$ and $^{15}NO_2$. The normal
frequencies in Table XXVIIIare adjusted to fit accura-
tely the product rule. If the mean-square amplitude
matrix elements at the absolute zero are concerned,
one has in accordance with equations (18) and (20)

4.4.

Table XXXI. Mean amplitudes of vibration in $^{14}NO_2$ and $^{15}NO_2$.

Molecule	Distance	Mean amplitude of vibration (Å)	
		T=0	298°K
$^{14}NO_2$	N–O	0.0382	0.0382
	O–O	0.0459	0.0469
$^{15}NO_2$	N–O	0.0378	0.0379
	O–O	0.0461	0.0469

$$\frac{\nu_1 \nu_2}{\nu_1^* \nu_2^*} = \frac{\Sigma_1 \Sigma_2 - \Sigma_{12}^2}{\Sigma_1^* \Sigma_2^* - (\Sigma_{12}^*)^2} = \left[\frac{(2\mu_X + \mu_Y)\mu_Y}{(2\mu_X^* + \mu_Y^*)\mu_Y^*}\right]^{\frac{1}{2}},$$

$$\frac{\nu_3}{\nu_3^*} = \frac{\Sigma_3}{\Sigma_3^*} = \left[\frac{2\mu_X \sin^2 A + \mu_Y}{2\mu_X^* \sin^2 A + \mu_Y^*}\right]^{\frac{1}{2}}.$$

(4.39)

By inserting the appropriate atomic masses according
to $\mu_X = 1/14.00754$, $\mu_X^* = 1/15.00489$ and $\mu_Y = \mu_Y^*$
$= 1/16.00000$, and with the value $2A = 134°15'$, the
numerical results 1.0239 and 1.0227 are obtained for
the respective ratios of equations (39). Approximately
the interaction mean-square amplitudes may be neglected.
The first one of equations (39) then reduces to

$$\nu_1 \nu_2 / \nu_1^* \nu_2^* \approx \Sigma_1 \Sigma_2 / \Sigma_1^* \Sigma_2^* = 1.0290 .$$

(4.40)

4.5.

4.5. Treatment of tetrahedral XY_4 molecules[*]

A similar treatment to that of the preceding section has been performed for the tetrahedral XY_4 molecular model. Some of the theoretical results will here be presented, together with numerical computations for germanium tetrachloride.
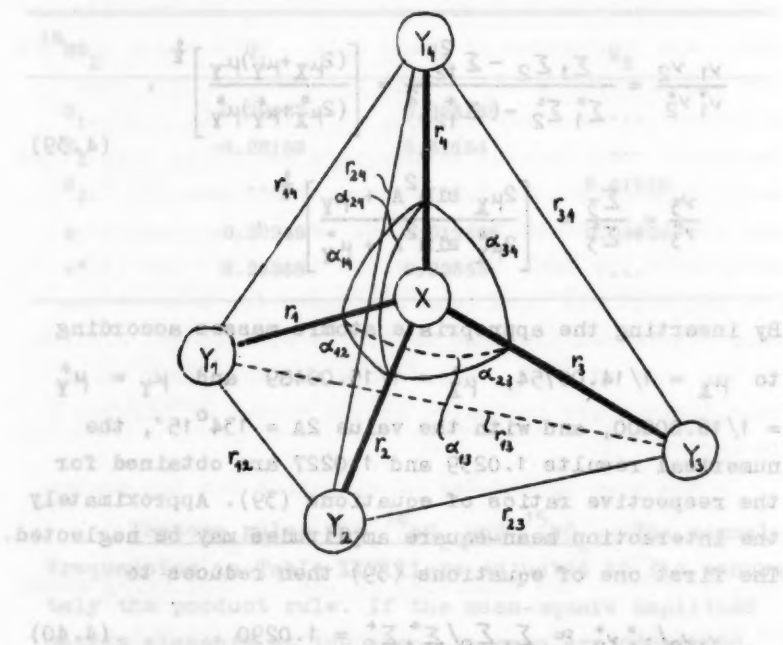
Fig.12. Notation used for the tetrahedral XY_4 molecular model (T_d). The symbols designate deviations from the equilibrium. The equilibrium X–Y bond length is identified by the symbol R.

[*] See also references [91], [111], [129], [102].

4.5.

Molecular symmetry. The considered molecular model (Fig. 12) has the T_d symmetry. The normal modes of vibration are distributed among the symmetrical species according to

$$\Gamma(Q) = A_1 + E + 2F_2 . \qquad (4.41)$$

In the following a complete set of symmetry coordinates is given, as formed by an orthogonal transformation from the valence force coordinates (see Fig.12).

Species A_1: $S_1 = \frac{1}{2}(r_1+r_2+r_3+r_4),$

Species E: $\begin{cases} S_{2a}= 12^{-\frac{1}{2}}R(2\alpha_{12}-\alpha_{23}-\alpha_{13}+2\alpha_{34}-\alpha_{14}-\alpha_{24}), \\ S_{2b}= \frac{1}{2}R(\alpha_{23}-\alpha_{13}+\alpha_{14}-\alpha_{24}), \end{cases}$

Species F_2: $\begin{cases} S_{3a}= 6^{-\frac{1}{2}}(r_1+r_2-2r_3), \\ S_{4a}= 12^{-\frac{1}{2}}R(2\alpha_{12}-\alpha_{23}-\alpha_{13}-2\alpha_{34}+\alpha_{14}+\alpha_{24}), \\ S_{3b}= 12^{-\frac{1}{2}}(r_1+r_2+r_3-3r_4), \\ S_{4b}= 6^{-\frac{1}{2}}R(\alpha_{12}+\alpha_{23}+\alpha_{13}-\alpha_{34}-\alpha_{14}-\alpha_{24}), \\ S_{3c}= 2^{-\frac{1}{2}}(r_2-r_1), \\ S_{4c}= \frac{1}{2}R(\alpha_{23}-\alpha_{13}-\alpha_{14}+\alpha_{24}). \end{cases}$

$$\qquad (4.42)$$

The following redundant coordinate of the species A_1 is present.

$$S_r = 6^{-\frac{1}{2}}R(\alpha_{12}+\alpha_{23}+\alpha_{13}+\alpha_{34}+\alpha_{14}+\alpha_{24}) \equiv 0 . \qquad (4.43)$$

It should be noticed that the angle displacements have been multiplied by the equilibrium distance R.

4.5.

Energy matrices and mean-square amplitude matrix.

The forms of the energy matrices of the considered type
of molecules have been reported several times. As for
the symmetrized G matrix in particular, references are
made to (91),(114),(101),(125),(102). Still it seems appropriate
to include the energy matrices here for conformity. The
symmetrized potential energy matrix is given by:

Species A_1 Species E Species F_2

$$\begin{array}{cccccc}
 & S_1 & S_2 & & S_3 & S_4 \\
F: & S_1\left[K_1\right] & S_2\left[\phi_2\right] & \begin{array}{c}S_3 \\ S_4\end{array} & \left[\begin{array}{cc}K_3 & \Gamma \\ & \phi_4\end{array}\right]
\end{array}$$

These force constants are given by

$$K_1 = k_0 + 3k_1 , \quad \phi_2 = f_0 - 2f_1 + f_2 ,$$

$$K_3 = k_0 - k_1 , \quad \phi_4 = f_0 - f_2 , \quad \Gamma = 2^{\frac{1}{2}}(g_0 - g_1), \qquad (4.44)$$

in terms of the valence force constants which enter into
the potential energy function (V), written in the following
way.

$$2V = k_0(r_1^2 + r_2^2 + r_3^2 + r_4^2) + 2k_1[r_1(r_2+r_3+r_4)+r_2(r_3+r_4)+r_3 r_4]$$

$$+ f_0 R^2 (\alpha_{12}^2 + \alpha_{23}^2 + \alpha_{13}^2 + \alpha_{34}^2 + \alpha_{14}^2 + \alpha_{24}^2)$$

$$+ 2f_1 R^2[\alpha_{12}(\alpha_{23}+\alpha_{13}+\alpha_{14}+\alpha_{24})+\alpha_{23}(\alpha_{13}+\alpha_{34}+\alpha_{24})$$

$$+\alpha_{13}(\alpha_{34}+\alpha_{14})+\alpha_{34}(\alpha_{14}+\alpha_{24})+\alpha_{14}\alpha_{24}]$$

4.5.

$$+ 2f_2R^2(\alpha_{12}\alpha_{34}+\alpha_{23}\alpha_{14}+\alpha_{13}\alpha_{24})$$

$$+ 2g_0R[r_1(\alpha_{12}+\alpha_{13}+\alpha_{14})+r_2(\alpha_{12}+\alpha_{23}+\alpha_{24})$$

$$+r_3(o_{23}+\alpha_{13}+\alpha_{34})+r_4(\alpha_{34}+\alpha_{14}+\alpha_{24})]$$

$$+ 2g_1R[r_1(\alpha_{23}+\alpha_{34}+\alpha_{24})+r_2(\alpha_{13}+\alpha_{34}+\alpha_{14})$$

$$+r_3(o_{12}+\alpha_{14}+\alpha_{24})+r_4(\alpha_{12}+\alpha_{23}+\alpha_{13})].$$

$$(4.45)$$

The symmetrized **G** matrix and its inverse will now be
given.

$$\qquad\qquad\qquad\qquad S_1 \qquad\qquad\qquad\qquad\qquad\qquad S_2$$

G : Species A_1: $S_1\left[\mu_Y\right]$ Species E: $S_2\left[3\mu_Y\right]$

$$\qquad\qquad\qquad\qquad\qquad S_3 \qquad\qquad S_4$$

$$\mathbf{G}: \text{Species } F_2: \quad \begin{matrix} S_3 \\ \\ S_4 \end{matrix}\begin{bmatrix} \tfrac{1}{3}(4\mu_X+3\mu_Y) & -\tfrac{4}{3}\mu_X \\ \\ & \tfrac{2}{3}(8\mu_X+3\mu_Y) \end{bmatrix}$$

$$\qquad\qquad\qquad\qquad S_1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad S_2$$

$$\mathbf{G}^{-1}: \text{Species } A_1: \ S_1\left[\mu_Y^{-1}\right] \quad \text{Species E: } S_2\left[\tfrac{1}{3}\mu_Y^{-1}\right]$$

Species F_2 $\qquad S_3 \qquad\qquad\qquad\qquad\qquad\qquad S_4$

$$\mathbf{G}^{-1}: \begin{matrix} S_3 \\ \\ S_4 \end{matrix}\begin{bmatrix} \tfrac{1}{3}(8\mu_X+3\mu_Y)(4\mu_X+\mu_Y)^{-1}\mu_Y^{-1} & \tfrac{4}{3}\mu_X(4\mu_X+\mu_Y)^{-1}\mu_Y^{-1} \\ \\ & \tfrac{1}{6}(4\mu_X+3\mu_Y)(4\mu_X+\mu_Y)^{-1}\mu_Y^{-1} \end{bmatrix}$$

4.5.

The symmetrized mean-square amplitude matrix is given by:

<table>
<tr><td>Species A_1</td><td>Species E</td><td colspan="2">Species F_2</td></tr>
<tr><td>S_1</td><td>S_2</td><td>S_3</td><td>S_4</td></tr>
<tr><td>$\Sigma: S_1 \left[\Sigma_1 \right]$</td><td>$S_2 \left[\Sigma_2 \right]$</td><td>$S_3$
S_4</td><td>$\begin{bmatrix} \Sigma_3 & \Sigma_{34} \\ & \Sigma_4 \end{bmatrix}$</td></tr>
</table>

One has

$$\Sigma_1 = \sigma_0 + 3\sigma_1 \ , \quad \Sigma_2 = \tau_0 - 2\tau_1 + \tau_2 \ ,$$
$$\Sigma_3 = \sigma_0 - \sigma_1 \ , \quad \Sigma_4 = \tau_0 - \tau_2 \ , \quad \Sigma_{34} = 2^{\frac{1}{2}}(\rho_0 - \rho_1), \tag{4.46}$$

where the entering quantities are defined by

$$\sigma_0 = \overline{r_1^2} \ , \qquad \sigma_1 = \overline{r_1 r_2} \ ,$$
$$\tau_0 = R^2 \overline{\alpha_{12}^2} \ , \quad \tau_1 = R^2 \overline{\alpha_{12}\alpha_{23}} \ , \quad \tau_2 = R^2 \overline{\alpha_{12}\alpha_{34}} , \tag{4.47}$$
$$\rho_0 = R \overline{r_1 \alpha_{12}} \ , \qquad \rho_1 = R \overline{r_1 \alpha_{23}} \ .$$

Because of the redundancy, some combinations of force constants are indeterminate, viz. $f_0 + 4f_1 + f_2$ and $g_0 + g_1$. Certain combinations of the mean-square amplitude quantities, however, are equal to zero. From the obvious relations

$$\overline{S_r^2} = 0 \ , \qquad \overline{S_r S_1} = 0 \ , \tag{4.48}$$

4.5.

S_r being the redundant coordinate [see equation (43)], and S_i an arbitrary coordinate, it is found

$$\tau_0 + 4\tau_1 + \tau_2 = 0 \;, \qquad \rho_0 + \rho_1 = 0 \;. \tag{4.49}$$

Normal frequencies. For the normal frequencies in terms of the λ values ($\lambda = 4\pi^2 \nu^2$) it is found

$$\lambda_1 = K_1 \mu_Y \;, \qquad\qquad \lambda_2 = 3\Phi_2 \mu_Y \;,$$

$$\lambda_3 + \lambda_4 = \tfrac{1}{3}K_3(4\mu_X + 3\mu_Y) + \tfrac{1}{3}\Phi_4(8\mu_X + 3\mu_Y) - \tfrac{16}{3}\Gamma\mu_X \;, \tag{4.50}$$

$$\lambda_3\lambda_4 = 2(K_3\Phi_4 - \Gamma^2)(4\mu_X + \mu_Y)\mu_Y \;.$$

The similar equations in terms of the Δ values $\left[\Delta = (h/8\pi^2\nu)\coth(h\beta\nu/2) \right]$ read

$$\Delta_1 = \Sigma_1\mu_Y^{-1} \;, \qquad \Delta_2 = \tfrac{1}{3}\Sigma_2\mu_Y^{-1} \;,$$

$$\Delta_3 + \Delta_4 = \tfrac{1}{3}\big[\Sigma_3(8\mu_X + 3\mu_Y) + \tfrac{1}{2}\Sigma_4(4\mu_X + 3\mu_Y)$$
$$\qquad\qquad\qquad + 8\Sigma_{34}\mu_X \big](4\mu_X + \mu_Y)^{-1}\mu_Y^{-1} \;, \tag{4.51}$$

$$\Delta_3\Delta_4 = \tfrac{1}{2}(\Sigma_3\Sigma_4 - \Sigma_{34}^2)(4\mu_X + \mu_Y)^{-1}\mu_Y^{-1} \;.$$

A set of relations similar to those of (35), involving both the force constants and the mean-square amplitude matrix elements, may also be established in the present case.

Connection with the central force coordinates. A set of central force coordinates is obtained from the valence

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force coordinates by replacing the Rα-type coordinates with the non-bonded distance deviations. Also a new set of symmetry coordinates may be established in terms of the central force coordinates as given in the following. For the notation, see Fig. 12 .

Species A_1: $\qquad S_1' = \frac{1}{2}(r_1 + r_2 + r_3 + r_4),$

Species E: $\begin{cases} S_{2a}' = 12^{-\frac{1}{2}}(2r_{12} - r_{23} - r_{13} + 2r_{34} - r_{14} - r_{24}), \\ S_{2b}' = \frac{1}{2}(r_{23} - r_{13} + r_{14} - r_{24}), \end{cases}$

Species F_2: $\begin{cases} S_{3a}' = 6^{-\frac{1}{2}}(r_1 + r_2 - 2r_3), \\ S_{4a}' = 12^{-\frac{1}{2}}(2r_{12} - r_{23} - r_{13} - 2r_{34} + r_{14} + r_{24}), \\ S_{3b}' = 12^{-\frac{1}{2}}(r_1 + r_2 + r_3 - 3r_4), \\ S_{4b}' = 6^{-\frac{1}{2}}(r_{12} + r_{23} + r_{13} - r_{34} - r_{14} - r_{24}), \\ S_{3c}' = 2^{-\frac{1}{2}}(r_2 - r_1), \\ S_{4c}' = \frac{1}{2}(r_{23} - r_{13} - r_{14} + r_{24}). \end{cases}$

$$(4.52)$$

An additional coordinate of the species A_1 must be included to achieve a complete orthogonal set, viz.

$$S_1^* = 6^{-\frac{1}{2}}(r_{12} + r_{23} + r_{13} + r_{34} + r_{14} + r_{24}). \qquad (4.53)$$

With this notation, the redundant condition may be written

$$2S_1' - S_1^* \equiv 0 . \qquad (4.54)$$

Consider the transformation

$$S' = A S , \qquad (4.55)$$

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where S and S' are column matrices containing the
coordinates of equations (42) and (55), respectively.
The transformation matrix is given by:

$$
A: \quad
\begin{array}{c}
 \\
S_1' \\
S_2' \\
S_3' \\
S_4'
\end{array}
\begin{array}{cccc}
S_1 & S_2 & S_3 & S_4 \\
\end{array}
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 3^{-\frac{1}{2}} & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & \tfrac{1}{3}3^{\frac{1}{2}} & 3^{-\frac{1}{2}}
\end{bmatrix}
$$

The energy matrices and the mean-square amplitude matrix
in terms of the new symmetry coordinates may be deter-
mined by transformations of the corresponding matrices
in terms of the original symmetry coordinates, according
to the following scheme.

$$
F' = \widetilde{A}^{-1} F A^{-1}, \qquad G' = A G \widetilde{A},
$$
$$
(G^{-1})' = \widetilde{A}^{-1} G^{-1} A^{-1}, \qquad \Sigma' = A \Sigma \widetilde{A}. \tag{4.56}
$$

In particular, the mean-square amplitude matrix in
terms of the new symmetry coordinates will be studied,
and is given by:

$$
\Sigma' : \quad
\begin{array}{cc}
\text{Species } A_1 & \text{Species } E \\
S_1' & S_2' \\
S_1' \begin{bmatrix} \Sigma_1' \end{bmatrix} & S_2' \begin{bmatrix} \Sigma_2' \end{bmatrix}
\end{array}
\quad
\begin{array}{c}
\text{Species } F_2 \\
\begin{array}{cc} S_3' & S_4' \end{array} \\
\begin{array}{c} S_3' \\ S_4' \end{array}
\begin{bmatrix} \Sigma_3' & \Sigma_{34}' \\ & \Sigma_4' \end{bmatrix}
\end{array}
$$

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One has [cf. equation (46)]

$$\Sigma_1' = \sigma_0' + 3\sigma_1' , \qquad \Sigma_2' = \tau_0' - 2\tau_1' + \tau_2' ,$$

$$\Sigma_3' = \sigma_0' - \sigma_1' , \quad \Sigma_4' = \tau_0' - \tau_2' , \quad \Sigma_{34}' = 2^{\pm}(\rho_0' - \rho_1'),$$

(4.57)

where

$$\sigma_0' = \overline{r_1^2} , \qquad \sigma_1' = \overline{r_1 r_2} ,$$

$$\tau_0' = \overline{r_{12}^2} , \qquad \tau_1' = \overline{r_{12} r_{23}} , \qquad \tau_2' = \overline{r_{12} r_{34}}, \quad (4.58)$$

$$\rho_0' = \overline{r_1 r_{12}} , \qquad \rho_1' = \overline{r_1 r_{23}} .$$

In accordance with the redundant condition (54) one has

$$4(\sigma_0' + 3\sigma_1') + (\tau_0' + 4\tau_1' + \tau_2') - 4(\rho_0 + \rho_1')6^{\pm} = 0 ,$$

(4.59)

$$4(\sigma_0' + 3\sigma_1') - (\tau_0' + 4\tau_1' + \tau_2') = 0 .$$

From the last one of relations (56) together with the equations of (46), the following expressions are found for the matrix elements of equations (57), in terms of the previously introduced quantities.

$$\Sigma_1' = \sigma_0 + 3\sigma_1 , \qquad \Sigma_2' = \tfrac{1}{3}(\tau_0 - 2\tau_1 + \tau_2) ,$$

$$\Sigma_3' = \sigma_0 - \sigma_1 , \quad \Sigma_{34}' = \tfrac{2}{3}3^{\pm}(\sigma_0 - \sigma_1) + \tfrac{1}{3}6^{\pm}(\rho_0 - \rho_1) , \quad (4.60)$$

$$\Sigma_4' = \tfrac{1}{3}(\sigma_0 - \sigma_1) + \tfrac{1}{3}(\tau_0 - \tau_2) + \tfrac{1}{3}2^{\pm}(\rho_0 - \rho_1) .$$

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Interatomic distance deviations. There exist two
types of interatomic distances in the considered case,
the distance deviations being represented by

$$r = r_4 , \qquad r^* = r_{12} = \tfrac{1}{3}6^{\tfrac{1}{2}}(r_1+r_2) + 3^{-\tfrac{1}{2}}R\alpha_{12} . \qquad (4.61)$$

In terms of the symmetry coordinates of equations (42)
one has

$$r = \tfrac{1}{2}S_1 - \tfrac{1}{2}3^{\tfrac{1}{2}}S_{3b} ,$$

$$r^* = \tfrac{1}{3}6^{\tfrac{1}{2}}S_1 + \tfrac{1}{3}S_{2a} + \tfrac{2}{3}(S_{3a}+2^{-\tfrac{1}{2}}S_{3b}) + \tfrac{1}{3}(S_{4a}+2^{-\tfrac{1}{2}}S_{4b}) . \qquad (4.62)$$

The mean-square amplitudes of vibration for the
bonded and non-bonded distances, viz. $u^2_{X-Y} = \overline{r^2}$ and
$u^2_{Y\cdots Y} = \overline{(r^*)^2}$, are expressed by the previously intro-
duced matrix elements in the following way. For the nota-
tion, see equations (58) and (47).

$$\overline{r^2} = \sigma_0' = \sigma_0 ,$$

$$\overline{(r^*)^2} = \tau_0' = \tfrac{1}{3}(\sigma_0+\sigma_1)+\tfrac{1}{18}(5\tau_0-4\tau_1-\tau_2)+\tfrac{2}{3}2^{\tfrac{1}{2}}(\varrho_0-\varrho_1). \qquad (4.63)$$

Simple approximations for germanium tetrachloride.
In the simple approximations (cf. section 4.3) specified
below, and which are going to be illustrated by computa-
tions for germanium tetrachloride, the harmonic vibrational
constants are determined by two given quantities.

(a) Simple valence force field approximation (SVF-f). A
sort of a simple valence force field approximation is
assumed by putting $K_1 = K_3$, $\phi_2 = \phi_4$ and $\Gamma = 0$, i.e.
$k_1 = 0$, $f_1 = f_2$ and $g_0 = g_1$. For the notation it is

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referred to equations (44) and (45).

(b) <u>Simple valence force mean-square amplitudes approximation at absolute zero</u> (SVF-a,0). In this case the mean-square amplitude matrix at the absolute zero point, its elements having been specified in equations (46), is assumed to have the form $\Sigma_1 = \Sigma_3$, $\Sigma_2 = \Sigma_4$, $\Sigma_{34} = 0$. These conditions may be expressed in terms of the quantities of equations (47) as $\sigma_1 = 0$, $\tau_1 = \tau_2$, $\rho_0 = \rho_1$.

(c) <u>Simple valence force mean-square amplitudes approximation at 298 $^{\circ}$K</u> (SVF-a,298). The conditions defined in (b) are assumed for the mean-square amplitude quantities at the temperature of 298 $^{\circ}$K.

(d) <u>Simple central force field approximation</u> (SCF-f). In this case, the approximations analogous to those of the case (a) are assumed for the potential energy matrix elements based on the central force coordinates. In accordance, the present approximation is found to be defined by $K_1 = K_3 + 4\phi_4 - 4\Gamma$, $\phi_2 = \phi_4$, $\Gamma - 2\phi_4 = 0$.

(e) <u>Simple central force mean-square amplitudes approximation at absolute zero</u> (SCF-a,0). In analogy with the case (b) it is assumed for the mean-square amplitude matrix elements given by equations (60) and at the absolute zero point: $\Sigma_1' = \Sigma_3'$, $\Sigma_2' = \Sigma_4'$ and $\Sigma_{34}' = 0$. It is possible to define this approximation in terms of the quantities of equations (46) in the following way:
$$\Sigma_1 = \Sigma_3, \quad \Sigma_2 = 4\Sigma_3 + \Sigma_4 + 4\Sigma_{34}, \quad 2\Sigma_3 + \Sigma_{34} = 0 .$$

(f) <u>Simple central force mean-square amplitudes approximation at 298 $^{\circ}$K</u> (SCF-a,298). The conditions of (e) are assumed for the mean-square amplitude quantities at 298 $^{\circ}$K.

In the present calculations the experimental

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Table XXXII. Calculated and observed vibrational frequencies of germanium tetrachloride (cm^{-1} units).

Species	A_1	E	F_2	
No.	1	2	3	4
(a)	397.0 [a])	132.0 [a])	515.4	142.4
(b)	397.0 [a])	132.0 [a])	713.5	144.6
(c)	397.0 [a])	132.0 [a])	571.0	142.3
(d)	397.0 [a])	132.0 [a])	524.8	140.1
(e)	397.0 [a])	132.0 [a])	788.7	130.8
(f)	397.0 [a])	132.0 [a])	588.5	139.3
Obs. [b])	397	132	452	171

[a]) Used in the calculations.   [b]) See reference [100].

values [100] for the frequencies ν_1 and ν_2 were used, and are quoted in Table XXXII The numerical results for the force constants [see equations (44)] and the mean-square amplitude matrix elements [see equations (46)] are given in Table XXXIII. In Table XXXII, the calculated frequencies ν_3 and ν_4 by the approximations here concerned, are included.

From the calculated frequencies (Table XXXII) it may be concluded that the approximations in the force field, viz. (a) and (d), are somewhat better than the corresponding approximations among the mean-square amplitudes, viz. (b) and (e), or (c) and (f), respectively. This superiority, however, is not very substantial. As a whole it must be concluded that the simple approximations

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Table XXXIII. Calculated force constants and mean-square amplitude quantities of germanium tetrachloride by the simple approximations (a) – (f).

(a)–(f)	Force constants (mdyneÅ^{-1})		Mean-square amplitudes (Å^2) T = 0	298 °K
κ_1	3.2912	Σ_1	0.0011979	0.0016116
ϕ_2	0.12128	Σ_2	0.010809	0.035076

(a)	Force constants (mdyneÅ^{-1})		Mean-square amplitudes (Å^2) T = 0	298 °K
κ_3	3.2912	Σ_3	0.0015287	0.0018253
ϕ_4	0.12128	Σ_4	0.012462	0.035643
Γ	0	Σ_{34}	−0.0009402	−0.0004499

(b)	Force constants (mdyneÅ^{-1})		Mean-square amplitudes (Å^2) T = 0	298 °K
κ_3	5.4343	Σ_3	0.0011979	0.0015109
ϕ_4	0.18616	Σ_4	0.010809	0.030113
Γ	−0.47506	Σ_{34}	0	0.0020852

(c)	Force constants (mdyneÅ^{-1})		Mean-square amplitudes (Å^2) T = 0	298 °K
κ_3	3.0509	Σ_3	0.0013889	0.0016116
ϕ_4	0.12400	Σ_4	0.012243	0.035076
Γ	−0.05204	Σ_{34}	−0.0007476	0

(d)	Force constants (mdyneÅ^{-1})		Mean-square amplitudes (Å^2) T = 0	298 °K
κ_3	3.7763	Σ_3	0.0015146	0.0018238
ϕ_4	0.12128	Σ_4	0.013683	0.040661
Γ	0.24256	Σ_{34}	−0.0015989	−0.0029586

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Table XXXIII (Continued).

(e)	Force constants $(mdyne\text{Å}^{-1})$		Mean-square amplitudes (Å^2)	
			$T = 0$	298 $^\circ$K
κ_3	9.3227	Σ_3	0.0011979	0.0017924
ϕ_4	0.24256	Σ_4	0.015600	0.050546
Γ	1.21465	Σ_{34}	−0.0023959	−0.0068045

(f)	Force constants $(mdyne\text{Å}^{-1})$		Mean-square amplitudes (Å^2)	
			$T = 0$	298 $^\circ$K
κ_3	4.7988	Σ_3	0.0013646	0.0016116
ϕ_4	0.12669	Σ_4	0.013828	0.041522
Γ	0.33428	Σ_{34}	−0.0016047	−0.0032231

having been applied, are not very good, a greater accuracy
being claimed in the majority of practical cases. Hence
the results given in Table XXXIII have not great value.

It is interesting to notice the large differences
between the mean-square amplitude approximations at
$T = 0$ and 298 $^\circ$K, respectively. These differences would
be smaller for molecules with higher normal frequencies,
but nevertheless the mentioned temperature-dependent
approximations seem to be somewhat arbitrary.

Modified approximations for germanium tetrachloride.
Another set of two-constant approximations could be
carried out by using the experimental values of ν_3 and
ν_4 in the calculations (instead of ν_1 and ν_2 in the case
above), but it would hardly be worthwhile to do this work.
A better idea is to bring the calculations to be consis-

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tent with all the observed frequencies ([100]) by making
allowance for some non-vanishing interaction terms.
Such calculations are reported in the present paragraph,
the following cases having been concerned:

(g) Modified valence force field approximation (MVF-f).

(h) Modified valence force mean-square amplitudes
approximation at 298 $^{\circ}$K (MVF-a,298).

(i) Modified central force field approximation (MCF-f).

(j) Modified central force mean-square amplitudes
approximation at 298 $^{\circ}$K (MCF-a,298).

These cases are modifications of the approximations
treated before, and specified by the following condi-
tions.

(g) MVF-f: $\Gamma = 0$.

(h) MVF-a,298: $\Sigma_{34} = 0$ for the mean-square amplitude
at 298 $^{\circ}$K.

(i) MCF-f: $\Gamma - 2\phi_4 = 0$.

(j) MCF-a,298: $3^{\frac{1}{2}}\Sigma_{34}' = 2\Sigma_3 + \Sigma_{34} = 0$ for the mean-
square amplitudes at 298 $^{\circ}$K.

Also the assumptions corresponding to (h) and (j) for
the mean-square amplitudes at the absolute zero point
were tried, but gave imaginary vibrational constant
values.

In the following calculations it will not be
possible to discuss the mutual superiorities of the
different cases by checking the calculated frequencies,
since all the observed frequencies will be reproduced
accurately by the calculations. Compared to the simple
approximations, however, an essential improvement will

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Table XXXIV. Calculated force constants and mean—square
amplitude quantities of germanium tetrachloride by the
modified approximations (g) — (j).

(g)—(j)	Force constants $(\text{mdyne}Å^{-1})$		Mean—square amplitudes $(Å^2)$ $T = 0$	$298\ ^\circ K$
K_1	3.2912	Σ_1	0.0011979	0.0016116
ϕ_2	0.12128	Σ_2	0.010809	0.035076

(g)	Force constants $(\text{mdyne}Å^{-1})$		Mean—square amplitudes $(Å^2)$ $T = 0$	$298\ ^\circ K$
K_3	2.4520	Σ_3	0.0017629	0.0022655
ϕ_4	0.17985	Σ_4	0.010366	0.024594
Γ	0	Σ_{34}	−0.0009042	−0.0004577

(h)	Force constants $(\text{mdyne}Å^{-1})$		Mean—square amplitudes $(Å^2)$ $T = 0$	$298\ ^\circ K$
K_3	2.3504	Σ_3	0.0017875	0.0023478
ϕ_4	0.18364	Σ_4	0.010082	0.023642
Γ	−0.04684	Σ_{34}	−0.0008577	0

(i)	Force constants $(\text{mdyne}Å^{-1})$		Mean—square amplitudes $(Å^2)$ $T = 0$	$298\ ^\circ K$
K_3	3.0257	Σ_3	0.0018112	0.0024272
ϕ_4	0.19711	Σ_4	0.011969	0.029970
Γ	0.39422	Σ_{34}	−0.0020956	−0.0041516

(j)	Force constants $(\text{mdyne}Å^{-1})$		Mean—square amplitudes $(Å^2)$ $T = 0$	$298\ ^\circ K$
K_3	3.1565	Σ_3	0.0019064	0.0027467
ϕ_4	0.23121	Σ_4	0.012334	0.031196
Γ	0.53742	Σ_{34}	−0.0024957	−0.0054934

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be achieved.

The numerical results for the force constants and mean-square amplitude matrix elements are listed in Table XXXIV. Only the most reliable one of the two sets of solutions, arising from the quadratic secular equation, are included.[*])

Force constants of the species F_2 for germanium tetrachloride. The three force constants of the triply degenerate species cannot be determined without ambiguity from the two normal frequencies. To obtain real values for the force constants, consistent with the observed frequencies ν_3 and ν_4 (Table XXXII), the following condition must be fulfilled for the interaction force constant in mdyne A^{-1}:

$$-0.31560 \leqslant \Gamma \leqslant 1.3908 .$$

All the possible force constant values over this range are represented by the ellipse in Fig. 13, the same procedure having been followed as previously for nitrogen dioxide (see Fig.9). The results from the approximations (g)-(j) (See Table XXXIV) are indicated on the diagram.

Mean-square amplitudes of the species F_2 for germanium tetrachloride. The three mean-square amplitude matrix elements of the triply degenerate species, viz. Σ_3, Σ_4 and Σ_{34}, at 298 °K are represented by the ellipse of Fig. 14 (cf. Fig. 10 for nitrogen dioxide). The restriction for the interaction mean-square amplitude in A^2 units is

$$-0.013490 \leqq \Sigma_{34} \leqq 0.0024996 .$$

The results from the approximations (g)-(j) (see Table XXXIV) are indicated on the diagram.

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[*]) For other calculations, see [61], [63], [125], [103], [99].

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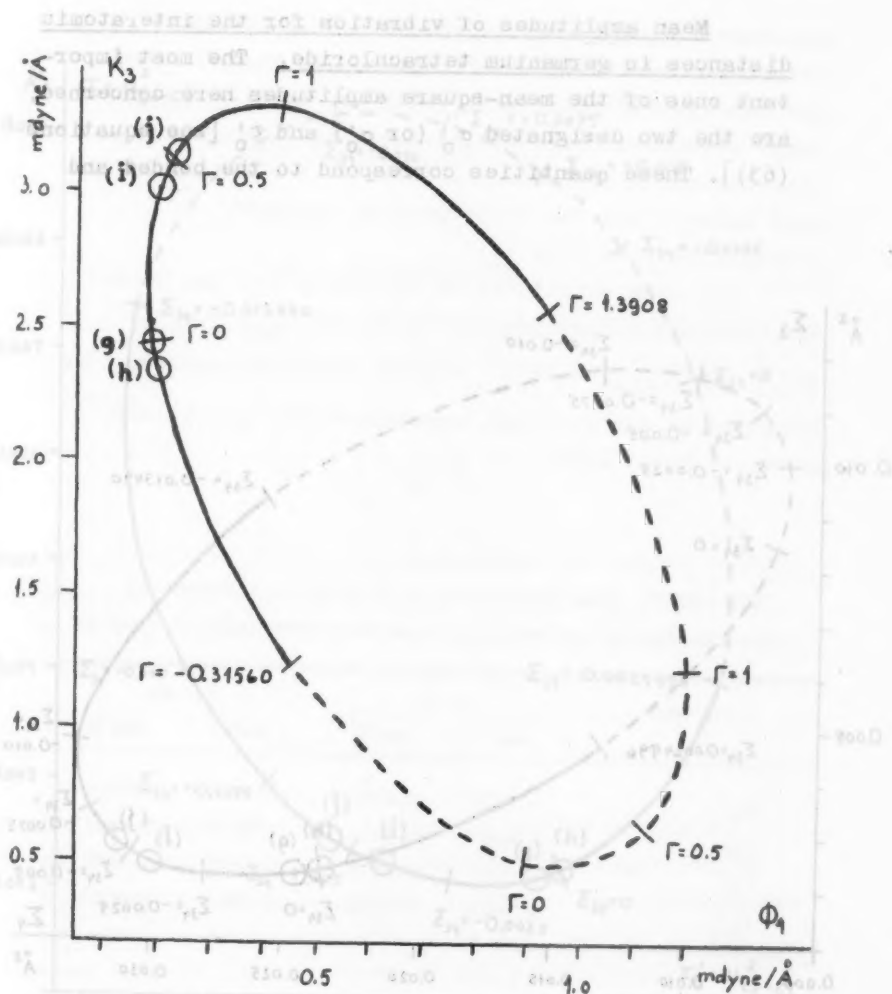
Fig.13. Force constants for germanium tetrachloride, consistent
with the observed frequencies. (g): MVF-f; (h): MVF-a,298; (i):
MCF-f; (j): MCF-a,298.

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Mean amplitudes of vibration for the interatomic distances in germanium tetrachloride.

The most important ones of the mean-square amplitudes here concerned, are the two designated σ_o (or σ_o') and τ_o' [see equations (63)]. These quantities correspond to the bonded and
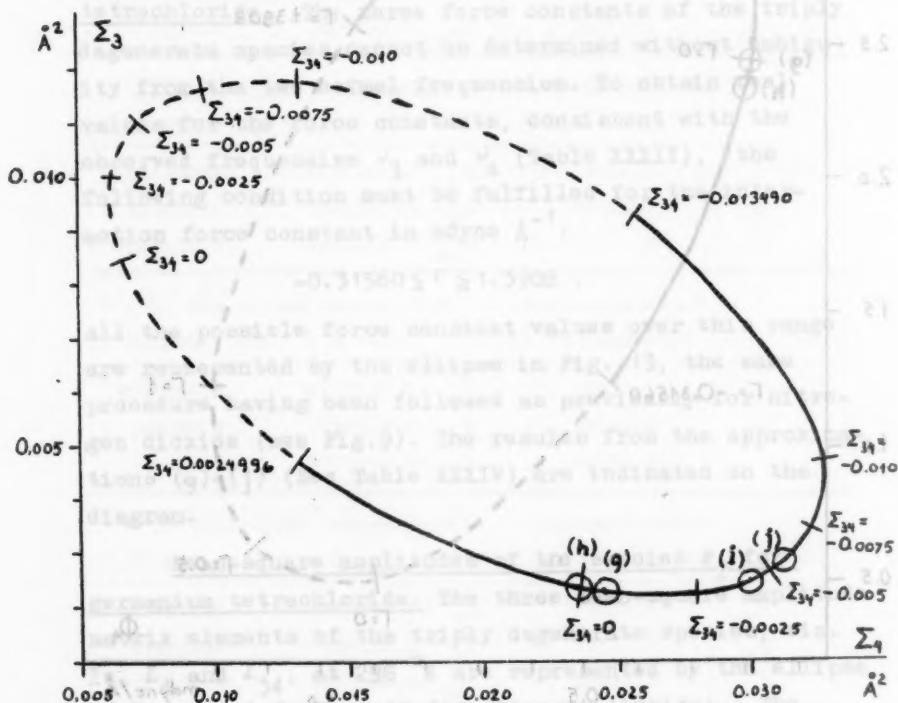
Fig. 14. Mean-square amplitude matrix elements at 298 ^{o}K for germanium tetrachloride, consistent with the observed frequencies. (g): MVF-τ; (h): MVF-a,298; (i): MCF-τ; (j): MCF-a,298.

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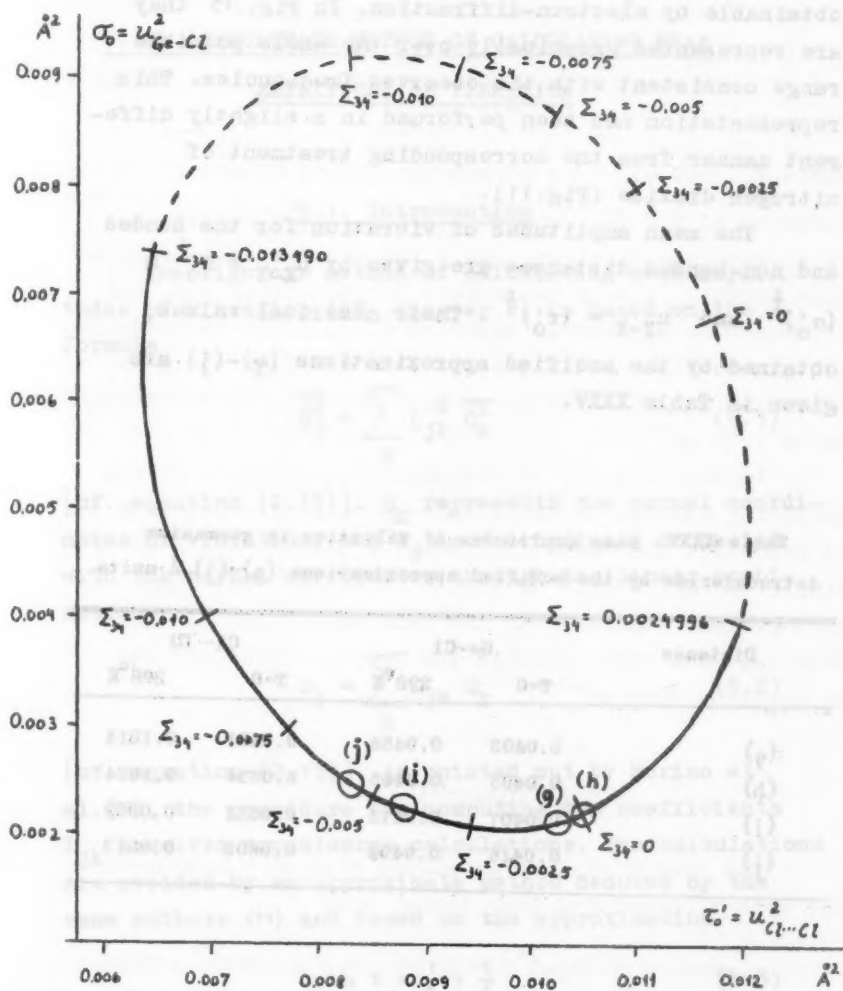
Fig. 15 . Mean-square amplitudes of vibration at 298 °K for germanium tetrachloride, consistent with the observed frequencies. (g): MVF-f; (h): MVF-a,298; (i): MCF-f; (j): MCF-a,298.

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non-bonded distances, respectively, and are also
obtainable by electron-diffraction. In Fig. 15 they
are represented graphically over the whole possible
range consistent with the observed frequencies. This
representation has been performed in a slightly diffe-
rent manner from the corresponding treatment of
nitrogen dioxide (Fig.11).

   The mean amplitudes of vibration for the bonded
and non-bonded distances are given by $u_{X-Y} = \sigma_0^{\frac{1}{2}} =$
$(\sigma_0')^{\frac{1}{2}}$ and $u_{Y\cdots Y} = (\tau_0')^{\frac{1}{2}}$. Their numerical values,
obtained by the modified approximations (g)-(j) are
given in Table XXXV.

Table XXXV. Mean amplitudes of vibration in germanium
tetrachloride by the modified approximations (g)-(j). Å units.

Distance	Ge—Cl		Cl···Cl	
	T=0	298°K	T=0	298°K
(g)	0.0403	0.0458	0.0651	0.1014
(h)	0.0405	0.0465	0.0656	0.1024
(i)	0.0407	0.0472	0.0617	0.0939
(j)	0.0416	0.0496	0.0605	0.0913

5. AN APPROXIMATE METHOD OF CALCULATING MEAN

AMPLITUDES OF VIBRATION

5.1. Introduction

The rigorous method of calculating mean ampli-
tudes of vibration (cf. chapter 2) is based on the
formula

$$\overline{S_j^2} = \sum_k L_{jk}^2 \overline{Q_k^2} \qquad (5.1)$$

[cf. equation (2.15)]. Q_k represents the normal coordi-
nates of vibration, and S_j is a coordinate connected
with the normal coordinates through the linear combi-
nation

$$S_j = \sum_k L_{jk} Q_k \qquad (5.2)$$

[cf. equation (2.13)]. As pointed out by Morino et
al.(⁹⁸), the procedure for computing the coefficients
L_{jk} involves troublesome calculations. The calculations
are avoided by an approximate method deduced by the
same authors (⁹⁸) and based on the approximation

$$\coth t = \frac{1}{t} + \frac{t}{4} \qquad (5.3)$$

for the hyperbolic cotangent which enters into the

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expression for $\overline{Q_k^2}$ of equation (1) according to equation (2.14). The derived approximate formula reads

$$\overline{S_j^2} = kT\, F_{jj}^{-1} + \frac{h^2}{64\pi^2 kT}\, G_{jj}\,, \qquad (5.4)$$

where F_{jj}^{-1} and $G_{jj} = \mu + \mu'$ are the proper diagonal elements of the F^{-1} and G matrices, respectively, k is Boltzmann's constant, and T the absolute temperature. This formula is very convenient for practical use, but it cannot be applied in cases of vibrational frequencies above about 1200 cm^{-1}. The reported error in the mean amplitude of vibration is up to 4 percent for frequencies below 1200 cm^{-1}.

In this chapter, a refinement of Morino's method including further terms in the approximation for coth t, is reported. The resulting formulae are not quite so simple as the formula of Morino et al.(4), but they give greater accuracy for the mean amplitudes of vibration and have been adjusted for ranges of frequencies up to about 3000 cm^{-1}.

5.2. Theory *)

The theory will be developed with an approximation for coth t containing four terms, viz.

$$\text{coth } t = -\theta_{-3} t^{-3} + \theta_{-1} t^{-1} + \theta_1 t - \theta_3 t^3. \quad (5.5)$$

---

*) For the original publications, see (44),(37),(38).

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The θ's are constants, which may be adjusted in correspondence to the range of vibrational frequencies.

Let Λ and Δ denote diagonal matrices, with the elements along the principal diagonals respectively

$$\lambda_k = 4\pi^2 \nu_k^2 \qquad (5.6)$$

and

$$\Delta_k = \overline{q_k^2} = (h/8\pi^2\nu_k)\coth(h\nu_k/2kT) \qquad (5.7)$$

[cf. equations (2.18),(4.4),(2.14) and (4.9)]. By introducing the approximation (5) with $t=h\nu_k/2kT$ in equation (7) and making use of the relation (6), the following formula is obtained,

$$\Delta = -\delta\Lambda^{-1}\Lambda^{-1}+\gamma\Lambda^{-1}+\alpha E -\beta\Lambda. \qquad (5.8)$$

Here

$$\alpha = \frac{h^2\theta_1}{16\pi^2 kT}, \qquad \beta = \frac{h^4\theta_3}{256\pi^4 (kT)^3}$$

$$\gamma = \theta_{-1} kT, \qquad \delta = \frac{16\theta_{-3}\pi^2(kT)^3}{h^2}. \qquad (5.9)$$

The transformation (2) may be written

$$S = L Q \qquad (5.10)$$

in matrix notation, where S and Q are column matrices. Hence the expression for the mean-square amplitude of vibration, equation (1), becomes

5.2.

$$\overline{s_j^2} = (L \Delta \tilde{L})_{jj} . \tag{5.11}$$

By inserting equation (8) and making use of the relations (2.17), the matrix L may be eliminated with the result

$$\overline{s_j^2} = -\delta(FGF)_{jj}^{-1} + \gamma F_{jj}^{-1} + \alpha G_{jj} - \beta(GFG)_{jj}. \tag{5.12}$$

Compared with Morino's approximate formula [see equation (4)], two additional terms appear in equation (12). Consequently, the whole F and G matrices must be known, and in addition to a few matrix multiplications, an inversion is implied.

Because of the diagonalization of the matrices, the calculations will be greatly facilitated when S_j [see equations (2) and (10)] are chosen as symmetry coordinates.

Let the desired mean-square amplitude of vibration be denoted by $\overline{r_i^2}$. It will now be assumed that r_i does not occur among the set of internal coordinates S_j used for setting up the F and G matrices which enter into equation (12). In such cases, the transformation

$$r_i = \sum_j U_{ij} S_j \tag{5.13}$$

is very useful. In matrix notation it can be written

$$r_i = \tilde{U}_i S = \tilde{U}_i L Q , \tag{5.14}$$

where U_i is the column matrix formed by the coefficients U_{ij}. Consequently, the formula for the mean-square

5.2.

amplitude of vibration, similar to equation (11),
reads

$$\overline{r_i^2} = \tilde{U}_i(L \Delta \tilde{L})U_i, \qquad (5.15)$$

and after elimination of L in the same way as
previously, yields the following result.

$$\overline{r_i^2} = -\delta \tilde{U}_i(FGF)^{-1}U_i + \gamma \tilde{U}_i F^{-1}U_i$$
$$+ \alpha \tilde{U}_i G U_i - \beta \tilde{U}_i(GFG)U_i . \qquad (5.16)$$

5.3. Numerical constants

Adjustment of the θ's. The constants θ of
equation (5) were adjusted by a least-squares method.
The following four intervals of t were chosen for
working out the four-constant approximations:

$$I \quad t = 0.5-4.0 ,$$
$$II \quad t = 1.0-5.5 ,$$
$$III \quad t = 1.5-6.5 ,$$
$$IV \quad t = 2.0-7.5 .$$

Which of these intervals should be applied for the
calculation of a mean amplitude of vibration in a
given case, depends on the magnitude of the normal
frequencies contributing to the vibration in question.
The approximations for coth t are given in Table XXXVI
where also Morino's approximation [see equation (3)]
is included. The deviations from coth t are found to
lie within about ± 1 percent by the four-constant

5.3.

Table XXXVI. Mathematical approximations for coth t.

t	coth t	Morino[a])	I [b])	II[c])	III[d])	IV[e])
0.1	10.033	10.025				
0.5	2.164	2.125	2.164			
1.0	1.313	1.250	1.323	1.310		
1.5	1.105	1.042	1.095	1.120	1.101	
2.0	1.037	1.000	1.027	1.031	1.053	1.032
2.5	1.014	1.025	1.013	1.000	1.014	1.023
3.0	1.005	1.083	1.013	0.996	0.997	1.006
3.5	1.002		1.010	1.003	0.993	0.994
4.0	1.001		0.991	1.011	0.998	0.991
4.5	1.000			1.014	1.004	0.992
5.0	1.000			1.008	1.010	0.996
5.5	1.000			0.988	1.011	1.000
6.0	1.000				1.006	1.003
6.5	1.000				0.993	1.003
7.0	1.000					0.999
7.5	1.000					0.989

a) $(1/t) + (t/4)$.

b) $\theta_1 = 0.267$, $\theta_3 = 0.00540$, $\theta_{-1} = 1.076$, $\theta_{-3} = 0.0151$.

c) $\theta_1 = 0.211$, $\theta_3 = 0.00246$, $\theta_{-1} = 1.310$, $\theta_{-3} = 0.208$.

d) $\theta_1 = 0.170$, $\theta_3 = 0.00133$, $\theta_{-1} = 1.665$, $\theta_{-3} = 0.875$.

e) $\theta_1 = 0.139$, $\theta_3 = 0.000770$, $\theta_{-1} = 2.074$, $\theta_{-3} = 2.215$.

approximation, corresponding to about ± 0.5 percent error in the mean amplitude of vibration.

Tabulation of numerical constants. The constants α, β, γ, and δ have been enumerated according

5.3.

Table XXXVII. Numerical constants for calculating mean amplitudes of vibration. *)

I	$(t = 0.5-4.0)$	$10^2\alpha$	$10^3\beta$	$10^2\gamma$	$10^5\delta$
T=273	$(190-1519 \text{ cm}^{-1})$	1.18576	2.82449	0.40573	0.48344
298	$(207-1658 \text{ cm}^{-1})$	1.08634	2.17192	0.44287	0.62870
323	$(225-1797 \text{ cm}^{-1})$	1.00230	1.70584	0.48000	0.80048

II	$(t = 1.0-5.5)$	$10^2\alpha$	$10^3\beta$	$10^2\gamma$	$10^4\delta$
T=273	$(380-2088 \text{ cm}^{-1})$	0.93706	1.28671	0.49397	0.66594
298	$(414-2279 \text{ cm}^{-1})$	0.85849	0.98943	0.53918	0.86602
323	$(449-2471 \text{ cm}^{-1})$	0.79208	0.77710	0.58439	1.10264

III	$(t = 1.5-6.5)$	$10^2\alpha$	$10^3\beta$	$10^2\gamma$	$10^3\delta$
T=273	$(570-2468 \text{ cm}^{-1})$	0.75498	0.69566	0.62783	0.28014
298	$(622-2694 \text{ cm}^{-1})$	0.69168	0.53494	0.68529	0.36431
323	$(674-2920 \text{ cm}^{-1})$	0.63817	0.42014	0.74275	0.46385

IV	$(t = 2.0-7.5)$	$10^2\alpha$	$10^3\beta$	$10^2\gamma$	$10^3\delta$
T=273	$(759-2848 \text{ cm}^{-1})$	0.61731	0.40275	0.78206	0.70916
298	$(829-3108 \text{ cm}^{-1})$	0.56555	0.30970	0.85363	0.92223
323	$(898-3369 \text{ cm}^{-1})$	0.52180	0.24324	0.92521	1.17421

*) Based on the following physical constants:
$c = 2.997929.10^{10}$ cm sec^{-1}, N(Avogadro's number) =
$6.02472.10^{23}$, $h = 6.6252.10^{-27}$ erg sec,
$k = 1.38042.10^{-16}$ erg degree^{-1} .

5.3.

to equations (9) for each of the approximations I
IV and at the temperatures $T = 273$, 298 and 323 °K.
The numerical values are given in Table XXXVII. To
obtain the mean-square amplitude of vibration in A^2
units, mdyne A^{-1} and atomic weight units should be
applied to the force constants and the masses, which
enter into the elements of the F and G matrices, respec-
tively.

5.4. Application to mean-square amplitude
matrices

The hyperbolic cotangent approximations reported
in the present chapter may also be applied for computing
the complete mean-square amplitude matrix Σ, given by

$$\Sigma = L \Delta \tilde{L} \qquad (5.17)$$

[cf. equation (4.10)]. Another mean-square amplitude
matrix, being connected with the set of quantities r_i
[see equations (13) and (14)] will be given by

$$P = U\Sigma\tilde{U} = U L \Delta \tilde{L} \tilde{U}. \qquad (5.18)$$

By using Morino's approximation (3) for elimina-
ting the L matrix, the following expressions are deduced
for the respective mean-square amplitude matrices.

$$\Sigma = kT F^{-1} + \frac{h^2}{64\pi^2 kT} G, \qquad (5.19)$$

$$P = kT U F^{-1} \tilde{U} + \frac{h^2}{64\pi^2 kT} U G \tilde{U}. \qquad (5.20)$$

5.4.

With the refined approximation for the hyper-
bolic cotangent, viz. equation (5), the corresponding
equations read

$$\Sigma = -\delta(FGF)^{-1} + \gamma F^{-1} + \alpha G - \beta GFG, \qquad (5.21)$$

$$P = -\delta U(FGF)^{-1}\tilde{U} + \gamma UF^{-1}\tilde{U} + \alpha UG\tilde{U}$$
$$- \beta UGFG\tilde{U}. \quad (5.22)$$

For a specific mean-square amplitude quantity, being
defined by

$$P_{ij} = \overline{r_i r_j}, \quad r_i = \tilde{U}_i S, \quad r_j = \tilde{U}_j S, \qquad (5.23)$$

one has

$$P_{ij} = -\delta \tilde{U}_i (FGF)^{-1} U_j + \gamma \tilde{U}_i F^{-1} U_j$$
$$+ \alpha \tilde{U}_i G U_j - \beta \tilde{U}_i GFG U_j. \quad (5.24)$$

Equation (16) represents the special case of equation
(24) with i = j.

5.5. Application to simple molecular models

In several cases of simple molecular models it is
convenient to express explicitly the approximate mean-
square amplitudes of vibration according to the described
method, in terms of the atomic masses and the force
constants.

In accordance with equations (12) and (16), the
matrices G, GFG, F^{-1} and $(FGF)^{-1}$ are to be
evaluated. However, the term containing the α coeffi-

5.5.

cient is always equal to $\alpha(\mu_X + \mu_Y)$, where μ_X and μ_Y denote the inverse masses of the adjacent atoms attached to the considered interatomic distance (98).

By evaluating the explicit formulae of mean-square amplitudes of vibration, the following scheme has showed to be useful: (i) Setting up the **G** and **F** matrices, (ii) determination of the corresponding inverse matrices, (iii) performing the matrix multiplications **GFG** and **F**$^{-1}$**G**$^{-1}$**F**$^{-1}$, (iv) expressing the interatomic displacements in terms of the chosen internal coordinates, and (v) determination of the terms of the mean-square amplitude formulae.

Some examples. The approximate mean-square amplitude formulae for the simple molecular models treated in the sections 2.2 and 4.2 may be derived straightforwardly. Such formulae, however, are supposed not to be practically important because of the simplicity of the rigorous formulae as given in Tables IV and XXV. On this place only some examples will be given, namely the expressions for linear symmetrical XY_2 molecules and for tetrahedral X_4 molecules. In the former case one has

$$u_{X-Y}^2 = \alpha(\mu_X+\mu_Y)-\tfrac{1}{2}\beta[(k+k')\mu_Y^2+(k-k')(2\mu_X+\mu_Y)^2]$$
$$+ \gamma k(k+k')^{-1}(k-k')^{-1}$$
$$-\tfrac{1}{2}\delta[(k+k')^{-2}\mu_Y^{-1} + (k-k')^{-2}(2\mu_X+\mu_Y)^{-1}] , \qquad (5.25)$$

$$u_{Y\cdots Y}^2 = 2\alpha\mu_Y - 2\beta(k+k')\mu_Y^2 + 2\gamma(k+k')^{-1}$$
$$- 2\delta(k+k')^{-2}\mu_Y^{-1} . \qquad (5.25)$$

5.5.

Here the same designations have been used as those of
sections 2.2 and 4.2. [*]) In the case of tetrahedral
X_4 molecules it has been found

$$u^2 = 2\alpha\mu_X - \beta(\tfrac{4}{3}K_1 + \tfrac{1}{3}K_2 + 2K_3)\mu_X^2$$
$$+ \gamma(\tfrac{1}{6}K_1^{-1} + \tfrac{1}{3}K_2^{-1} + \tfrac{1}{2}K_3^{-1})$$
$$- \delta(\tfrac{1}{24}K_1^{-2} + \tfrac{1}{3}K_2^{-2} + \tfrac{1}{4}K_3^{-2})\mu_X^{-1} . \qquad (5.27)$$

In this equation the entering force constants are those
of the symmetrized potential energy matrix. The
connection with the previously used force constants
[see equation (2.46)] is

$$K_1 = k+4k'+k" , \quad K_2 = k-2k'+k" , \quad K_3 = k-k" . \qquad (5.28)$$

Linear triatomic molecules. The theoretical
treatment in the general case of linear triatomic
molecules is published elsewhere [40]. The cited paper
is concerned with the mean-square amplitude matrices,
and includes the final formulae for the approximate
mean-square amplitude quantities. In the present para-
graph a detailed evaluation of these formulae will be
presented.

Since the displacements to the first order
approximation are considered, only the parallel vibrations
need to be taken into account. Hence the vibrations are
described by the two interatomic distance deviations

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[*]) The reader should not be confused by the differing usage of
the symbol β.

5.5.
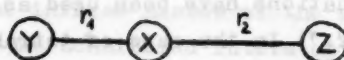
Fig. 16 . Linear triatomic YXZ molecular model ($C_{\infty v}$). The symbols r_1 and r_2 denote the deviations from the respective equilibrium distances.

defined by Fig.16 . In terms of these coordinates the F and G matrices are given by:

$$\mathbf{F}: \begin{array}{cc} & \begin{array}{cc} r_1 & r_2 \end{array} \\ \begin{array}{c} r_1 \\ r_2 \end{array} & \begin{bmatrix} k_1 & k' \\ & k_2 \end{bmatrix} \end{array} \qquad \mathbf{G}: \begin{array}{cc} & \begin{array}{cc} r_1 & r_2 \end{array} \\ \begin{array}{c} r_1 \\ r_2 \end{array} & \begin{bmatrix} \mu_X+\mu_Y & -\mu_X \\ & \mu_X+\mu_Z \end{bmatrix} \end{array}$$

The corresponding potential energy function is given by the equation

$$2V = k_1 r_1^2 + k_2 r_2^2 + 2k' r_1 r_2 . \qquad (5.29)$$

By inversion of the matrices, one obtains:

$$\mathbf{F^{-1}}: \begin{array}{cc} & \begin{array}{cc} r_1 & \qquad\qquad r_2 \end{array} \\ \begin{array}{c} r_1 \\ r_2 \end{array} & \begin{bmatrix} k_2/[k_1 k_2-(k')^2] & -k'/[k_1 k_2-(k')^2] \\ & k_1/[k_1 k_2-(k')^2] \end{bmatrix} \end{array}$$

5.5.

$$G^{-1}: \begin{array}{c} \\ r_1 \\ \\ r_2 \end{array} \begin{bmatrix} \overset{r_1}{\dfrac{\mu_X+\mu_Z}{\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X}} & \overset{r_2}{\dfrac{\mu_X}{\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X}} \\ \\ \dfrac{\mu_X+\mu_Y}{\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X} \end{bmatrix}$$

By matrix multiplication it is found

$$GFG = \begin{bmatrix} a & c \\ & b \end{bmatrix}, \qquad F^{-1}G^{-1}F^{-1} = \begin{bmatrix} A & C \\ & B \end{bmatrix}, \qquad (5.30)$$

where

$$a = k_1(\mu_X+\mu_Y)^2 + k_2\mu_X^2 - 2k'(\mu_X+\mu_Y)\mu_X ,$$

$$b = k_1\mu_X^2 + k_2(\mu_X+\mu_Z)^2 - 2k'(\mu_X+\mu_Z)\mu_X ,$$

$$(5.31)$$

$$c = -k_1(\mu_X+\mu_Y)\mu_X - k_2(\mu_X+\mu_Z)\mu_X$$
$$+ k'[(\mu_X+\mu_Y)(\mu_X+\mu_Z)+\mu_X^2] ,$$

and

$$A = [k_2^2(\mu_X+\mu_Z) + (k')^2(\mu_X+\mu_Y) - 2k_2k'\mu_X]$$
$$\times [k_1k_2-(k')^2]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1} ,$$

$$B = [k_1^2(\mu_X+\mu_Y) + (k')^2(\mu_X+\mu_Z) - 2k_1k'\mu_X]$$
$$\times [k_1k_2-(k')^2]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1} ,$$

5.5.

$$C = \left\{ \left[k_1 k_2 + (k')^2\right]\mu_X - k_1 k' (\mu_X + \mu_Y) - k_2 k' (\mu_X + \mu_Z) \right\}$$
$$\times \left[k_1 k_2 - (k')^2\right]^{-2} (\mu_X \mu_Y + \mu_Y \mu_Z + \mu_Z \mu_X)^{-1} .$$

$$(5.32)$$

The interatomic distance deviations for the non-bonded atom pair, viz. $Y \cdots Z$, are given by

$$r^* = r_1 + r_2 . \qquad (5.33)$$

Hence all the mean-square amplitude quantities to be considered may be given as matrix elements by:

$$
\mathbf{P} : \quad
\begin{array}{c}
\\ r_1 \\ r_2 \\ r^*
\end{array}
\begin{array}{ccc}
r_1 & r_2 & r^* \\
\left[\begin{array}{ccc}
\sigma_1 & \sigma' & \sigma_1'^* \\
 & \sigma_2 & \sigma_2'^* \\
 & & \sigma^*
\end{array} \right]
\end{array}
$$

Let one of the matrices $\mathbf{G}$, $\mathbf{GFG}$, $\mathbf{F}^{-1}$ and $(\mathbf{FGF})^{-1}$ be denoted

$$\mathbf{H} = \begin{bmatrix} x & z \\ & y \end{bmatrix} . \qquad (5.34)$$

According to equation (24), the following expressions are required for computing the $\mathbf{P}$ matrix elements,

$$\tilde{U}_1 H U_1 = x , \qquad \tilde{U}_2 H U_2 = y ,$$
$$\tilde{U}_1 H U_2 = z , \qquad \tilde{U}^* H U^* = x+y+2z , \qquad (5.35)$$
$$\tilde{U}_1 H U^* = x+z , \qquad \tilde{U}_2 H U^* = y+z .$$

5.5.

In these equations

$$U_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad U_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad U^* = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{5.36}$$

The final expressions for $\sigma_1 = \overline{r_1^2}$, $\sigma_2 = \overline{r_2^2}$ and $\sigma^* = \overline{(r^*)^2}$ are included in Table XXVIII. For the off-diagonal elements of the P matrix, i.e. the interaction mean-square amplitudes, the following results have been deduced.

$$\sigma' = -\alpha\mu_X$$
$$+\beta\left[(k_1+k_2-2k')\mu_X^2+(k_1-k')\mu_X\mu_Y+(k_2-k')\mu_X\mu_Z-k'\mu_Y\mu_Z\right]$$
$$-\gamma k'\left[k_1k_2-(k')^2\right]^{-1}$$
$$-\delta\left[(k_1-k')(k_2-k')\mu_X-k_1k'\mu_Y-k_2k'\mu_Z\right]$$
$$\times\left[k_1k_2-(k')^2\right]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1}, \tag{5.37}$$

$$\sigma_1'^* = \alpha\mu_Y$$
$$-\beta\left[(k_1-k')\mu_X\mu_Y-(k_2-k')\mu_X\mu_Z+k_1\mu_Y^2+k'\mu_Y\mu_Z\right]$$
$$+\gamma(k_2-k')\left[k_1k_2-(k')^2\right]^{-1}$$
$$-\delta\left[(k_2-k')(k_1+k_2-2k')\mu_X+k_2(k_2-k')\mu_Z-k'(k_1-k')\mu_Y\right]$$
$$\times\left[k_1k_2-(k')^2\right]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1}, \tag{5.38}$$

5.5.

$$\sigma_2^{'*} = \alpha \mu_Z$$

$$- \beta \left[(k_2-k')\mu_X\mu_Z - (k_1-k')\mu_X\mu_Y + k_2\mu_Z^2 + k'\mu_Y\mu_Z \right]$$

$$+ \gamma(k_1-k')\left[k_1 k_2 - (k')^2 \right]^{-1} +$$

$$-\delta \left[(k_1-k')(k_1+k_2-2k')\mu_X + k_1(k_1-k')\mu_Y - k'(k_2-k')\mu_Z \right]$$

$$\times \left[k_1 k_2 - (k')^2 \right]^{-2} (\mu_X\mu_Y + \mu_Y\mu_Z + \mu_Z\mu_X)^{-1} .$$

$$(5.39)$$

Linear symmetrical X_2Y_2 molecules. The approximate formulae for the mean-square amplitudes of vibration of the four types of interatomic distances are included in Table XXXVIII. To define the entering force constants, the linear part of the harmonic potential energy function is given below.

$$2V = k_1(r_1^2+r_2^2) + 2k_1'r_1r_2 + k_2 d^2 + 2k_2'(r_1+r_2)d . \quad (5.40)$$

For the coordinates here applied, see Fig. 17.
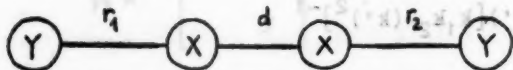
Fig.17. Linear symmetrical X_2Y_2 molecule model $(D_{\infty h})$. The symbols denote the respective interatomic displacements.

5.5.

Plane symmetrical XY_3 molecules. This molecular model has been treated extensively in section 2.3. The same notation [see especially equations (2.53)] has been used by evaluating the approximate formulae, which are given in Table XXXVIII.

Tetrahedral XY_4 molecules. For an extensive theoretical treatment of this molecular model, reference is made to section 4.5. The evaluated approximate formulae for the mean-square amplitudes of vibration are given in Table XXXVIII.

Table XXXVIII. Mean-square amplitudes of vibration of simple molecular models. III. *) Approximate formulae.

Molecule	Distance	Mean-square amplitude of vibration
Linear YXZ	X—Y	$\alpha(\mu_X+\mu_Y)$
		$-\beta\left[(k_1+k_2-2k')\mu_X^2+k_1\mu_Y^2+2(k_1-k')\mu_X\mu_Y\right]$
		$+\gamma k_2\left[k_1k_2-(k')^2\right]^{-1}$
		$-\delta\left[(k_2-k')^2\mu_X + k_2^2\mu_Z + (k')^2\mu_Y\right]$
		$\times\left[k_1k_2-(k')^2\right]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1}$
	X—Z	$\alpha(\mu_X+\mu_Z)$
		$-\beta\left[(k_1+k_2-2k')\mu_X^2 + k_2\mu_Z^2 + 2(k_2-k')\mu_X\mu_Z\right]$
		$+\gamma k_1\left[k_1k_2-(k')^2\right]^{-1}$
		$-\delta\left[(k_1-k')^2\mu_X + k_1^2\mu_Y + (k')^2\mu_Z\right]$
		$\times\left[k_1k_2-(k')^2\right]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1}$

5.5.

Table XXXVIII (Continued).

	Y→Z	$\alpha(\mu_Y+\mu_Z)$
		$-\beta(k_1\mu_Y^2 + k_2\mu_Z^2 + 2k'\mu_Y\mu_Z)$
		$+\gamma(k_1+k_2-2k')[k_1k_2-(k')^2]^{-1}$
		$-\delta[(k_1+k_2-2k')^2\mu_X+(k_1-k')^2\mu_Y+(k_2-k')^2\mu_Z]$
		$\times [k_1k_2-(k')^2]^{-2}(\mu_X\mu_Y+\mu_Y\mu_Z+\mu_Z\mu_X)^{-1}$

	X-Y	$\alpha(\mu_X+\mu_Y)$
Linear sym.X_2Y_2		
		$-\beta[(k_1+k_2-2k_2')\mu_X^2 + k_1\mu_Y^2 + 2(k_1-k_2')\mu_X\mu_Y]$
		$+\frac{1}{2}\gamma\left\{(k_1-k_1')^{-1}+k_2[(k_1+k_1')k_2-2(k_2')^2]^{-1}\right\}$
		$-\frac{1}{2}\delta\left\{(k_1-k_1')^{-2}(\mu_X+\mu_Y)^{-1}+[(k_2-k_2')^2\mu_X+(k_2')^2\mu_Y]\right.$
		$\left.\times[(k_1+k_1')k_2-2(k_2')^2]^{-2}(\mu_X\mu_Y)^{-1}\right\}$

	X-X	$2\alpha\mu_X - 2\beta(k_1+k_1'+2k_2-4k_2')\mu_X^2$
		$+\gamma(k_1+k_1')[(k_1+k_1')k_2-2(k_2')^2]^{-1}$
		$-\frac{1}{2}\delta[(k_1+k_1'-2k_2')^2\mu_X + (k_1+k_1')^2\mu_Y]$
		$\times [(k_1+k_1')k_2-2(k_2')^2]^{-2}(\mu_X\mu_Y)^{-1}$

	X··Y	$\alpha(\mu_X+\mu_Y)$
		$-\beta[(k_1+k_2-2k_2')\mu_X^2+k_1\mu_Y^2 - 2(k_1'-k_2')\mu_X\mu_Y]$
		$+\frac{1}{2}\gamma\left\{(k_1-k_1')^{-1} + [2(k_1+k_1') + k_2 - 4k_2']\right.$
		$\left.\times [(k_1+k_1')k_2-2(k_2')^2]^{-1}\right\}$

5.5.

Table XXXVIII (Continued).

$$-\tfrac{1}{2}\delta\left\{(k_1-k_1')^{-2}(\mu_X+\mu_Y)^{-1}\right.$$

$$+\left[(k_1+k_1'+k_2-3k_2')^2\mu_X+(k_1+k_1'-k_2')^2\mu_Y\right]$$

$$\left.\times\left[(k_1+k_1')k_2-2(k_2')^2\right]^{-2}(\mu_X\mu_Y)^{-1}\right\}$$

$Y\cdots Y$ $2\alpha\mu_Y - 2\beta(k_1+k_1')\mu_Y^2$

$$+\gamma(k_1+k_1'+2k_2-4k_2')[(k_1+k_1')k_2-2(k_2')^2]^{-1}$$

$$-\tfrac{1}{2}\delta[(k_1+k_1'+2k_2-4k_2')^2\mu_X + (k_1+k_1'-2k_2')^2\mu_Y]$$

$$\times[(k_1+k_1')k_2-2(k_2')^2]^{-2}(\mu_X\mu_Y)^{-1}$$

Plane $X-Y$ $\alpha(\mu_X+\mu_Y)$
sym.XY_3

$$-\beta\left[\tfrac{3}{2}(K_2+3\phi+12^{\tfrac{1}{2}}\Gamma)\mu_X^2 + \tfrac{1}{3}(K_1+2K_2)\mu_Y^2\right.$$

$$\left.+ 2(K_2+3^{\tfrac{1}{2}}\Gamma)\mu_X\mu_Y\right]$$

$$+\tfrac{1}{3}\gamma[K_1^{-1} + 2\phi(K_2\phi-\Gamma^2)^{-1}]$$

$$-\tfrac{1}{3}\delta\left\{K_1^{-2}\mu_Y^{-1} + [(3^{\tfrac{1}{2}}\phi+\Gamma)^2\mu_X + \tfrac{2}{3}(3\phi^2+\Gamma^2)\mu_Y]\right.$$

$$\left.\times(K_2\phi-\Gamma^2)^{-2}(3\mu_X+\mu_Y)^{-1}\mu_Y^{-1}\right\}$$

$Y\cdots Y$ $2\alpha\mu_Y - \beta[K_1 + \tfrac{1}{2}(K_2+3\phi) + 3^{\tfrac{1}{2}}\Gamma]\mu_Y^2$

$$+\gamma[K_1^{-1} + \tfrac{1}{6}(K_2+3\phi+12^{\tfrac{1}{2}}\Gamma)(K_2\phi-\Gamma^2)^{-1}]$$

$$-\delta\left\{K_1^{-2}\mu_Y^{-1} + \tfrac{1}{6}[\tfrac{1}{2}(K_2+3\phi+12^{\tfrac{1}{2}}\Gamma)^2\mu_X\right.$$

$$+\tfrac{1}{3}(K_2+3^{\tfrac{1}{2}}\Gamma)^2\mu_Y + \tfrac{1}{3}(3\phi+3^{\tfrac{1}{2}}\Gamma)^2\mu_Y]$$

$$\left.\times(K_2\phi-\Gamma^2)^{-2}(3\mu_X+\mu_Y)^{-1}\mu_Y^{-1}\right\}$$

5.5.

Table XXXVIII (Continued).

Tetra-hedral XY_4	X–Y	$\alpha(\mu_X+\mu_Y)$
		$-\beta[\frac{1}{3}(K_3+4\phi_4-4\Gamma)\mu_X^2 + \frac{1}{4}(K_1+3K_3)\mu_Y^2$
		$+2(K_3-2\Gamma)\mu_X\mu_Y]$
		$+\frac{1}{4}\gamma[K_1^{-1} + 3\phi_4(K_3\phi_4-\Gamma^2)^{-1}]$
		$-\frac{1}{4}\delta\{K_1^{-2}\mu_Y^{-1} + [2(2\phi_4-\Gamma)^2\mu_X+\frac{3}{2}(2\phi_4^2+\Gamma^2)\mu_Y]$
		$\times (K_3\phi_4-\Gamma^2)^{-2}(4\mu_X+\mu_Y)^{-1}\mu_Y^{-1} \}$
	Y–Y	$2\alpha\mu_Y - \frac{1}{3}\beta(2K_1+3\phi_2+2K_3+2\phi_4+4\Gamma)\mu_Y^2$
		$+\frac{1}{3}\gamma[2K_1^{-1} + \frac{1}{3}\phi_2^{-1}$
		$+\frac{4}{2}(K_3+4\phi_4-4\Gamma)(K_3\phi_4-\Gamma^2)^{-1}]$
		$-\frac{1}{3}\delta\{(2K_1^{-2} +\frac{1}{9}\phi_2^{-2})\mu_Y^{-1}+[\frac{1}{3}(K_3+4\phi_4-4\Gamma)^2\mu_X$
		$+\frac{1}{4}(K_3-2\Gamma)^2\mu_Y+\frac{1}{2}(2\phi_4-\Gamma)^2\mu_Y]$
		$\times (K_3\phi_4-\Gamma^2)^{-2}(4\mu_X+\mu_Y)^{-1}\mu_Y^{-1} \}$

*) For I and II; see Tables IV and XXV.

Numerical examples. In this paragraph some numerical results will be presented for the mean amplitudes of vibration of some simple molecules, calculated by the described approximation method.

When the same molecular constants are used as previously for $^{11}BF_3$ (see Table VI), the formulae given in Table XXXVIII lead to

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$$u_{B-P}^2 = 0.1434\alpha - 0.1648\beta + 0.1390\gamma - 0.1627\delta \,,$$
$$\hspace{9cm}(5.41)$$
$$u_{P\cdots P}^2 = 0.1053\alpha - 0.03371\beta + 0.4518\gamma - 2.6948\delta \,.$$

Here the numerical values are based on atomic weight
units for the masses, and mdyne $\mathring{A}^{-1}$ for the force cons-
tants. After a glance on the magnitudes of the frequencies
(480.4 - 1453.5 cm^{-1}; Table VI), it is seen from Table XXXVII
that both of the approximations I and II can be applied.
By a further inspection (Table VII) it is found that the
ν_4 vibration (1453.5 cm^{-1}) gives an almost negligible
contribution to the interatomic distance deviations for
a bonded atom pair (B-P). Hence the approximations III,
as well as IV (at least at the two lower temperatures
referred to in Table XXXVII), may also be expected to
give reliable results for u_{B-P}, but not for $u_{P\cdots P}$. The
computational results at 298 $^\circ$K given in Table XXXIX
show a perfect agreement with these predictions, if the
values are compared to those from rigorous calculations
($u_{B-P} = 0.0425 \,\mathring{A}$, $u_{P\cdots P} = 0.0552 \,\mathring{A}$; Table VIII). The
failure of the approximations III and IV for a non-bonded
atom pair (P$\cdots$P) is demonstrated by the figures in
parantheses in Table XXXIX . All the other values for
$^{11}BP_3$ deviate less than 0.5 percent from the rigorous
ones.

In the application of the present method to
germanium tetrachloride, the force constant values from
the modified valence force field, referred to as (g)
in section 4.5, were used (see Table XXXIV). Then it was
found

5.5.

Table XXXIX. Approximate mean amplitudes of vibration at 298 ^{o}K for boron trifluoride ($^{11}BF_3$) and germanium tetrachloride (Å units).

Molecule	Distance	Approximation			
		I	II	III	IV
$^{11}BF_3$	B–F	0.0426	0.0425	0.0424	0.0424
	F–F	0.0553	0.0554	(0.0531)	(0.0442)
$GeCl_4$	Ge–Cl	0.0459	(0.0452)	(0.0367)	
	Cl–Cl	(0.0994)			

$$u^2_{Ge-Cl} = 0.04198\alpha - 0.004825\beta + 0.3818\gamma - 4.2662\delta ,$$

$$(5.42)$$

$$u^2_{Cl\cdots Cl} = 0.05641\alpha - 0.003237\beta + 2.3173\gamma - 157.41\delta .$$

The lowest vibrational frequencies of germanium tetrachloride (Table XXXII) are seen to fall outside the ranges being encountered for in Table XXXVII. It may be realized, however, that the interatomic distance deviations for a bonded atom pair(Ge–Cl) depend mainly on ν_1 and ν_3. Hence the approximation I may be expected to give reliable results for u_{Ge-Cl} (cf. Table XXXIX). Morino's approximation (4) applied to this case gives $u_{Ge-Cl} = 0.0447$ Å and $u_{Cl\cdots Cl} = 0.1006$ Å at 298 ^{o}K, these values deviating -2.4 and -0.8 percent, respectively, from the rigorously calculated values ($u_{Ge-Cl} = 0.0458$ Å, $u_{Cl\cdots Cl} = 0.1014$ Å; Table XXXV).

5.6.

5.6. Application to a molecule of the plane symmetrical XY_2Z type

The mean amplitudes of vibration of some molecules of the type to be considered here, have been studied by Bakken,[*] from whose thesis some of the numerical values in this section have been taken. A theoretical treatment of the vibrations of XY_2Z type molecules has also been given by Venkateswarlu and Sundaram [127]. For some approximate calculations of mean amplitudes of vibration, including those for formaldehyde, this being the molecule to be concerned here, reference is made to a paper of Cyvin and Bakken [44].

<u>Molecular symmetry.</u> The planar vibrations of the molecular model here considered (Fig. 18) are described by the five internal coordinates given on the figure. For the symmetry properties of the normal modes of vibration it is found

$$\Gamma(Q) = 3A_1 + 2B_1 + B_2 . \tag{5.43}$$

The vibration belonging to the species B_2 is an out-of-plane motion.

The following symmetry coordinates have been formed.

Symm.species A_1: $\quad \left\{ \begin{array}{l} S_1 = q \\ S_2 = d \\ S_3 = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1 + \alpha_2) \end{array} \right.$

Symm.species B_1: $\quad \left\{ \begin{array}{l} S_4 = 2^{-\frac{1}{2}}(x_1 - x_2) \\ S_5 = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1 - \alpha_2) \end{array} \right.$

Notice that the angle displacement coordinates have been multiplied by $(RD)^{\frac{1}{2}}$, in order to have the same dimension to all the symmetry coordinates.

5.6.
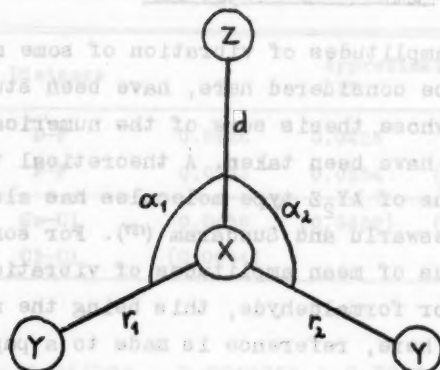
Fig.18. Notation used for the plane symmetrical XY_2Z molecular model (C_{2v}). The symbols denote the deviations from equilibrium values. The equilibrium lengths of the bonds X–Y and X–Z are designated R and D, respectively, and 2A is the equilibrium value of the YXY angle.

Sym. species A_1:
$$
\begin{cases}
S_1 = 2^{-\frac{1}{2}}(r_1+r_2) \ , \\
S_2 = d \ , \\
S_3 = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1+\alpha_2) \ ,
\end{cases}
$$
(5.44)

Sym. species B_1:
$$
\begin{cases}
S_4 = 2^{-\frac{1}{2}}(r_1-r_2) \ , \\
S_5 = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1-\alpha_2)
\end{cases}
$$

Notice that the angle displacement coordinates have been multiplied by $(RD)^{\frac{1}{2}}$, in order to have the same dimension to all the symmetry coordinates.

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Table XL. In-plane force constants for the plane symmetrical XY_2Z molecular model.

	r_1	r_2	d	$(RD)^{\frac{1}{2}}\alpha_1$	$(RD)^{\frac{1}{2}}\alpha_2$
r_1	k_r	k_r'	k_{rd}	$\varepsilon_{r\alpha}$	$\varepsilon_{r\alpha}'$
d			k_d	$\varepsilon_{d\alpha}$	$\varepsilon_{d\alpha}$
$(RD)^{\frac{1}{2}}\alpha_1$				f_α	f_α'

Energy matrices. The harmonic potential energy function contains nine force constants, given in Table XL. For the symmetrized potential energy matrix, see Table XLI.

Table XLI. The symmetrized in-plane potential energy matrix for the plane symmetrical XY_2Z molecular model.

		S_1	S_2	S_3
Species A_1	S_1	$k_r + k_r'$	$2^{\frac{1}{2}}k_{rd}$	$\varepsilon_{r\alpha} + \varepsilon_{r\alpha}'$
	S_2		k_d	$2^{\frac{1}{2}}\varepsilon_{d\alpha}$
	S_3			$f_\alpha + f_\alpha'$

		S_4	S_5
Species B_1	S_4	$k_r - k_r'$	$\varepsilon_{r\alpha} - \varepsilon_{r\alpha}'$
	S_5		$f_\alpha - f_\alpha'$

5.6.

Table XLII. Elements of the in-plane inverse kinetic energy matrix for the plane symmetrical XY_2Z molecular model.

	r_1	r_2	d
r_1	$\mu_X + \mu_Y$	$\mu_X \cos 2A$	$-\mu_X \cos A$
d			$\mu_X + \mu_Z$

	$(RD)^{\frac{1}{2}}\alpha_1$
r_1	$-(R/D)^{\frac{1}{2}}\mu_X \sin A$
d	$-(D/R)^{\frac{1}{2}}\mu_X \sin A$
$(RD)^{\frac{1}{2}}\alpha_1$	$(D/R)(\mu_X + \mu_Y) + (R/D)(\mu_X + \mu_Z) + 2\mu_X \cos A$

	$(RD)^{\frac{1}{2}}\alpha_2$
r_1	$[2(D/R)^{\frac{1}{2}}\cos A + (R/D)^{\frac{1}{2}}]\mu_X \sin A$
d	$-(D/R)^{\frac{1}{2}}\mu_X \sin A$
$(RD)^{\frac{1}{2}}\alpha_1$	$-(D/R)\mu_X \cos 2A - (R/D)(\mu_X + \mu_Z) - 2\mu_X \cos A$

The **G** matrix elements which correspond to the force constants of Table XL , may be determined by means of tabulated formulae (47), (136), and are given in Table XLII. μ_X, μ_Y and μ_Z denote as usual the inverse masses of the respective atoms. In Table XLIII , the elements of the symmetrized **G** matrix are tabulated.

Interatomic distance deviations. A set of four representative interatomic distance deviations in the

5.6.

considered molecular model (Fig. 18) is given below.

$$r = r_1 , \quad d , \quad t = (r_1 + r_2)\sin A - R(\alpha_1 + \alpha_2)\cos A ,$$
$$r^* = (R^2 + D^2 + 2RD\cos A)^{-\frac{1}{2}}[(R + D\cos A)r_1$$
$$+ (D + R\cos A)d + RD\alpha_1\sin A] . \tag{5.45}$$

In terms of the symmetry coordinates one has:

$$r = 2^{-\frac{1}{2}}(S_1 + S_4) , \quad d = S_2 ,$$
$$t = 2^{\frac{1}{2}}[S_1\sin A - (R/D)^{\frac{1}{2}}S_3\cos A] ,$$
$$r^* = (R^2 + D^2 + 2RD\cos A)^{-\frac{1}{2}}[2^{-\frac{1}{2}}(R + D\cos A)S_1$$
$$+ (D + R\cos A)S_2 + 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}S_3\sin A$$
$$+ 2^{-\frac{1}{2}}(R + D\cos A)S_4 + 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}S_5\sin A] . \tag{5.46}$$

Computation of the approximate mean-square ampli-
tudes of vibration. Let one of the matrices $\mathbf{G}, \mathbf{GFG}$,
$\mathbf{F}^{-1}$ and $(\mathbf{FGF})^{-1}$, based on the symmetry coordinates (44),
be represented by

$$\mathbf{H} = \begin{bmatrix} a & d & f & 0 & 0 \\ & b & e & 0 & 0 \\ & & c & 0 & 0 \\ & & & g & i \\ & & & & h \end{bmatrix} . \tag{5.47}$$

Then the following expressions are required for computing
the four mean-square amplitudes of vibration, according
to the described approximation method.

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$$\tilde{U}_1 H U_1 = \tfrac{1}{2}(a+g) , \qquad \tilde{U}_2 H U_2 = b ,$$

$$\tilde{U}_3 H U_3 = 2\left[a\sin^2 A + c(R/D)\cos^2 A - f(R/D)^{\frac{1}{2}}\sin 2A\right] ,$$

$$\tilde{U}_4 H U_4 = \left[1/(R^2+D^2+2RD\cos A)\right]\left[\tfrac{1}{2}(a+g)(R+D\cos A)^2\right.$$

$$+ b(D+R\cos A)^2 + \tfrac{1}{2}(c+h)RD\sin^2 A$$

$$+ 2^{\frac{1}{2}}d(R+D\cos A)(D+R\cos A)$$

$$+ 2^{\frac{1}{2}}e(D+R\cos A)(RD)^{\frac{1}{2}}\sin A$$

$$\left. + (f+i)(R+D\cos A)(RD)^{\frac{1}{2}}\sin A\right] .$$

(5.48)

In these equations, the column matrices U_1 are defined by

$$r = \tilde{U}_1 S , \quad d = \tilde{U}_2 S , \quad t = \tilde{U}_3 S , \quad r^* = \tilde{U}_4 S , \quad (5.49)$$

where S represents the symmetry coordinates (44), given as a column matrix, and determined by the transformation (46).

 Numerical computations for formaldehyde. The F and G matrices have been taken from Bakken's *) calculations, and are given numerically in the following. The applied units for the F and G matrix elements are mdyne A^{-1} and Awu, respectively.

$$\text{Species } A_1 \quad F: \quad \begin{matrix} & S_1 & S_2 & S_3 \\ S_1 & 4.5416 & 0 & 0 \\ S_2 & & 12.1909 & 0.5261 \\ S_3 & & & 1.1692 \end{matrix}$$

*) See footnote p. 23 . The calculations are based on data from Herzberg (44).

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Species B_1 $\quad$ F :

$$\begin{array}{c} & s_4 & s_5 \\ s_4 & \begin{bmatrix} 4.3492 & 0.06849 \\ s_5 & & 0.6176 \end{bmatrix} \end{array}$$

Species A_1 $\quad$ G :

$$\begin{array}{c} & s_1 & s_2 & s_3 \\ s_1 \\ s_2 \\ s_3 & \begin{bmatrix} 1.0295 & -0.05580 & 0.07431 \\ & 0.1458 & -0.1109 \\ & & 1.2824 \end{bmatrix} \end{array}$$

Species B_1 $\quad$ G :

$$\begin{array}{c} & s_4 & s_5 \\ s_4 \\ s_5 & \begin{bmatrix} 1.1212 & -0.2114 \\ & 1.5902 \end{bmatrix} \end{array}$$

The resulting formulae for the mean-square amplitudes of vibration are:

$$u_{C-H}^2 = 1.0753\alpha - 5.1578\beta + 0.2253\gamma - 0.04783\delta ,$$

$$u_{C-O}^2 = 0.1458\sigma - 0.2705\beta + 0.08365\gamma - 0.04955\delta ,$$

$$u_{H\cdot\cdot H}^2 = 1.9841\alpha - 7.5236\beta + 0.6839\gamma - 0.3248\delta ,$$ (5.50)

$$u_{H\cdot\cdot O}^2 = 1.0546\sigma - 3.4850\beta + 0.5137\gamma - 0.3781\delta .$$

Here the normal vibrations from both of the species (A_1 and B_1) contribute to the interatomic distance deviations for the C-H and H···O pairs, but only those from A_1 to C-O and H···H. The actual frequency ranges in these two cases are 1280 - 2874 cm^{-1} and 1503 - 2780 cm^{-1}, respectively. Both of these ranges are within the allowed

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Table XLIV. Approximate and rigorous mean amplitudes of
vibration at 298 $^{\circ}$K in formaldehyde (Å units).

Distance	Approximation				Rigorous[a])
	I	II	III	IV	
C–H	(0.0384)	(0.0731)	(0.0788)	0.0798	0.0801
C–O	0.0370	0.0373	0.0377	0.0375	0.0372
H··H	(0.0908)	(0.1151)	0.1194	0.1201	0.1170
H··O	(0.0785)	(0.0913)	(0.0939)	0.0944	0.0912

a) Reference (10).

interval for the approximation IV at 298 $^{\circ}$K (see Table
XXXVII), but also the approximation III will probably
give reasonable results for u_{C-O} and $u_{H\cdots H}$. Furthermore,
since the C–O distance deviations depend mainly on ν_2
(1503 cm^{-1}), probably also the approximations I and II
are applicable for u_{C-O}. The calculated results are
given in Table XLIV, together with the rigorously
calculated values (10). The percentage deviations are in
some cases unexpectedly large (especially for $u_{H\cdots H}$ and
$u_{H\cdots O}$ by approximation IV), but they still do not
exceed some few percent.

5.7.

5.7. Discussion

It may be stated that the accuracy (about 0.5 percent error) of the mean amplitudes of vibration based on the four-constant hyperbolic cotangent approximation, is sufficiently high for any practical purpose at present. Because of the inclusion of the two additional terms $(-\theta_{-3}t^{-3}$ and $-\theta_3 t^3)$, however, the approximate computations are not always simple. In fact the rigorous L matrix method may be preferred in many cases.

Still one advantage of the approximation method remains, namely the fact that the mean amplitudes of vibration for several simple molecular models may be expressed e x p l i c i t l y according to this method. Moreover, the approximate computations are rather perspicuous, although they may be laborious. Probably the approximation method may have some importance for machine solutions of mean amplitudes of vibration in the future.

6. THE USE OF MEAN AMPLITUDES OF VIBRATION IN

FORCE CONSTANT DETERMINATIONS

6.1. General introduction

Definition of vibrational constants. As stated previously (chapter 1), the rigid model of a polyatomic molecule of given symmetry in its equilibrium position, is defined by a certain number of parameters. To define the non-rigid model, an additional set of parameters are required, and will here be referred to as **v i b r a -
t i o n a l   c o n s t a n t s .** *) In addition, the term "complete set of vibrational constants" will be used to designate a set of independent vibrational cons-tants which are sufficient for defining the vibrating structure. Only small harmonic vibrations will here be concerned. Some examples of vibrational constants are given in the following.

(i) Normal frequencies. The set of normal frequen-cies for a polyatomic molecule usually represents an in-complete set of vibrational constants.

(ii) Force constants. A complete set of force constants (including all interaction terms) is a complete set of vibrational constants.

(iii) Mean amplitudes of vibration. The mean amplitude of vibration for any type of (bonded or non-

---

*) Confusion should be avoided, although the term "vibrational constant" is used in some different meanings in the literature.

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bonded) interatomic distance in a polyatomic molecule is a type of vibrational constants. The whole set may be complete or incomplete.

(iv) Mean-square amplitude quantities. If the mean-square amplitude matrix is based on a complete set of internal coordinates, its elements (i.e. the mean-square amplitudes of vibration and the interaction mean-square amplitudes) will represent a complete set of vibrational constants.

Discussion of the vibrational constants. A molecule with N atoms and no internal rotation will now be considered. Hence its whole intramolecular motion may be described by the vibrational modes. There exist:

N-1 linear vibrational modes for a linear molecule,

2N-3 in-plane vibrational modes for a planar molecule, and

3N-6 vibrational modes in the general case.

This will give the number of normal coordinates, as well as arbitrary internal coordinates of a complete set, which describes the vibrational modes. The number of normal frequencies may be decreased on account of the degeneracy, depending on molecular symmetry.

In general, the number of vibrational constants of a complete set is dependent on the molecular symmetry.[*]) In Table XLV some examples are shown. The

----

[*]) Let the normal modes be distributed among the symmetry species according to

$$\Gamma(Q) = \sum_{\gamma} n^{(\gamma)} \Gamma^{(\gamma)} , \quad \text{(Cont. p. 174)}$$

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Table XLV. Numbers of vibrational constants in specific molecular models.

Molecular model	Example	Normal frequencies [a]	Mean amplitudes [b]	Vibrational constants [a,c]
Diatomic	H_2, HCl	1	1	1
XY_2 ($D_{\infty h}$)	CO_2	2	2	2
XYZ ($C_{\infty v}$)	COS	3	3	3
XY_2 (C_{2v})	H_2O	3	2	4
X_4 (T_d)	P_4	2	1	3
X_2Y_2 ($D_{\infty h}$)	C_2H_2	3	4	4
XY_3 (D_{3h})	BCl_3	3	2	4
XY_3 (C_{3v})	NH_3	4	3	6
XY_2Z (C_{2v})	CH_2O	5	4	9
XY_4 (T_d)	CH_4	4	2	5
XY_3Z (C_{3v})	CH_3Cl	6	4	12
X_2Y_4 (V_h)	C_2H_4	6	6	15
Allene (V_h)	C_3H_4	11	7	23
Benzene (D_{6h})	C_6H_6	14	10	26
Cyclopropane (D_{3h})	C_3H_6	14	6	27
Cyclobutane (D_{4h})	(C_4H_8) [d]	23	10	43

[a] Only the linear vibrations for the linear molecules and in-plane vibrations for the planar molecules are taken into account.

6.1.

Table XLV (Continued).

b) Number of mean amplitudes of vibration for all the types of bonded and non-bonded atom pairs.

c) Number of vibrational constants of a complete set, according to the definition in the text.

d) Planar ring structure is assumed.

table contains also the number of normal frequencies in the specified molecular models, as well as the number of mean amplitudes of vibration for all the types of (bonded and non-bonded) interatomic distances. In principle, all the normal frequencies are obtainable from spectroscopic data, and the mean amplitudes of vibration from electron-diffraction data.

It should be pointed out that the considerations leading to the figures in Table XLV are rather schematic. In reality the situation is more complex in the majority of cases, for instance for the following reasons: (a) The normal frequencies of isotopically substituted molecules give some additional information which very often has great importance for the solution of the vibrational problem. (b) Practical difficulties frequently reduce the number of mean amplitudes of vibration

where the irreducible representations are denoted by $\Gamma^{(\gamma)}$. Then the number of vibrational constants in a complete set is given by

$$ s = \frac{1}{2} \sum_{\gamma} n^{(\gamma)} \left[n^{(\gamma)} + 1 \right] . $$

As an example, one has for the cyclopropane molecule according to equation (2.57):

$$ s = 6 + 1 + 10 + 1 + 3 + 6 = 27. $$

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obtainable by electron-diffraction, e.g. the impossi-
bility of resolving the peaks of the radial-distribution
curve for distances of nearly the same magnitude. (c)
Some ambiguities leading to alternative sets of vibra-
tional constants will occur when quadratic or still
higher-power secular equations are involved.

Nevertheless, the table tends to give an idea of
the nature of the particular problems, and the possibi-
lities to solve them by different methods.

Use of mean amplitudes of vibration in force
constant determinations. *) It is seen from the fore-
going discussion that the knowledge of some mean ampli-
tudes of vibration, obtained from electron-diffraction
measurements, may serve as additional information to the
normal frequencies from spectroscopic data, for deter-
mining the force constants of the molecule. The first
succeafull results in this field have been achieved
by Morino et al. (99), who studied the germanium tetra-
chloride and carbon tetrachloride molecules.

In the present chapter, the possibility will be
examined, of applying the mean amplitudes of vibration
for determining the complete harmonic force field of
the boron trifluoride molecule. Next the germanium tetra-
chloride molecule will be studied, and the usefullness
of the new secular equation method, described in chapter
4, will be demonstrated.

6.2. Discussion of the boron trifluoride molecule

For the theoretical treatment of the plane symmetri-

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*) See also section 1.5.

6.2.

cal XY_3 molecular model, reference is made to section 2.3.

Specification of the problem. For the in-plane vibrations of the planar symmetrical XY_3 molecules (see Table XLV) there are four harmonic force constants, of which three belong to the species E'. This species contains only two normal frequencies if a specific molecule is considered. Here the $^{11}BF_3$ molecule will be considered, and any constructued force field shall be adjusted to the vibrational frequencies quoted in Table VI. When this condition is fulfilled there still remains an ambiguity as to the three force constants of the E' species, since one additional piece of information is required for a complete determination of the force field. *) In the following, the influence on the force constants will be discussed, when various values of mean amplitudes of vibration are chosen.

Calculation of force constants for boron tri-fluoride. The frequency 888 cm^{-1} (Table VI) gives the value K_1 = 8.8236 mdyne A^{-1} without ambiguity for the force constant of the species A_1'. The solution for r e a l values for the force constants of the species E', viz. K_2, φ and Γ, limits the range allowed for each of them. From equations (2.52) the interaction constant Γ in mdyne A^{-1} units is found to be

$$-6.7036 \leqq \Gamma \leqq 0.35953 .$$

The force constant ellipse is reproduced in Fig. 19 (cf. Figs. 9 and 13). Some of the values on the full-

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*) In this argument the ambiguity in force constants arising from the quadratic secular equation has not been included.

6.2.
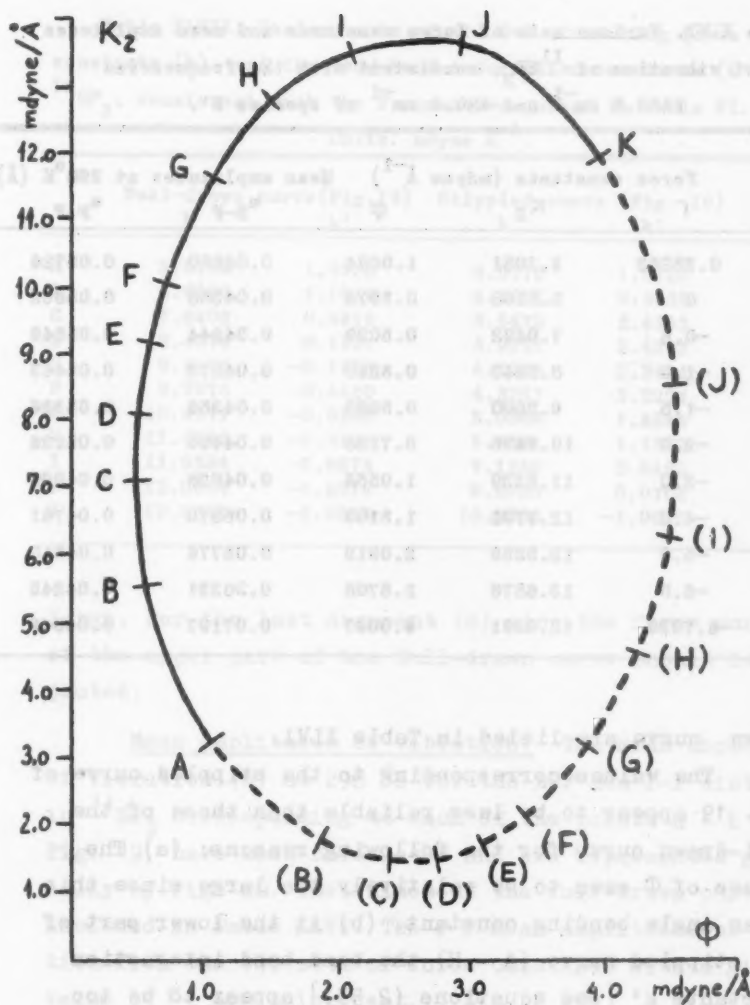
Fig. 19. Force constants for BF₃, consistent with the
frequencies 1453.5 cm⁻¹ and 480.4 cm⁻¹ of species E'.

6.2.

Table XLVI. Various sets of force constants and mean amplitudes
of vibration of $^{11}BF_3$, consistent with the frequencies
1453.5 cm^{-1} and 480.4 cm^{-1} of species E'.

	Force constants (mdyne Å^{-1})			Mean amplitudes at 298°K (Å)	
	Γ	K_2	ϕ	u_{B-F}	u_{F-F}
A	0.35953	3.2051	1.0684	0.04850	0.05726
B	0	5.5168	0.5973	0.04358	0.05652
C	-0.5	7.0492	0.5029	0.04244	0.05549
D	-1.0	8.2443	0.5210	0.04273	0.05443
E	-1.5	9.2600	0.5988	0.04359	0.05336
F	-2.0	10.1495	0.7188	0.04490	0.05226
G	-3.0	11.6339	1.0568	0.04838	0.04999
H	-4.0	12.7702	1.5109	0.05270	0.04761
I	-5.0	13.5259	2.0919	0.05776	0.04510
J	-6.0	13.6878	2.8708	0.06391	0.04245
K	-6.7036	12.0291	4.0097	0.07197	0.04049

drawn curve are listed in Table XLVI.

The values corresponding to the stippled curve of
Fig. 19 appear to be less reliable than those of the
full-drawn curve for the following reasons: (a) The
values of ϕ seem to be relatively too large since this
is an angle bending constant. (b) At the lower part of
the stippled curve (A - H) the bond-bond interaction
constants k' [see equations (2.53)] appear to be too
large in comparison with the respective B-F stretching
force constants k. For the numerical values, see Table
XLVII. (c) At the upper part of the curve the absolute
magnitudes of the interaction constant Γ are unreliably

6.2.

Table XLVII. Various sets of the B-F stretching force
constants (k), and the bond-bond interaction constants (k') of
$^{11}BF_3$, consistent with the frequencies quoted in Table VI.
Units: mdyne $Å^{-1}$.

| | Full-drawn curve(Fig.19) | | Stippled curve (Fig. 19) | |
	k	k'	k	k'
A	5.0779	1.8728	5.0779	1.8728
B	6.6190	1.1023	4.1357	2.3439
C	7.6406	0.5915	3.9470	2.4383
D	8.4374	0.1931	3.9831	2.4202
E	9.1146	−0.1455	4.1388	2.3424
F	9.7075	−0.4420	4.3787	2.2224
G	10.6971	−0.9368	5.0548	1.8844
H	11.4546	−1.3155	5.9631	1.4303
I	11.9584	−1.5674	7.1250	0.8493
J	12.0664	−1.6214	8.6828	0.0704
K	10.9606	−1.0685	10.9606	−1.0685

large. For the last argument (c) also the force constants
of the upper part of the full-drawn curve should be re-
jected.

Mean amplitudes of vibration. The mean amplitudes
of vibration (u) at 298 °K for the B-F and F··F distances
in $^{11}BF_3$ corresponding to each of the points A - K of
Fig. 19, have been calculated and are represented graphi-
cally by Fig. 20. The values of the full-drawn curve are
included in Table XLVI. The F··F mean amplitudes of vibra-
tion from the two sets of force constants with a given
value of Γ, are coincident.

By an inspection of Fig. 20, it is found that the
B-F mean amplitude of vibration in some instances is
unreliably large, compared to the corresponding F··F mean
amplitude of vibration. This is the case for the values

6.2.
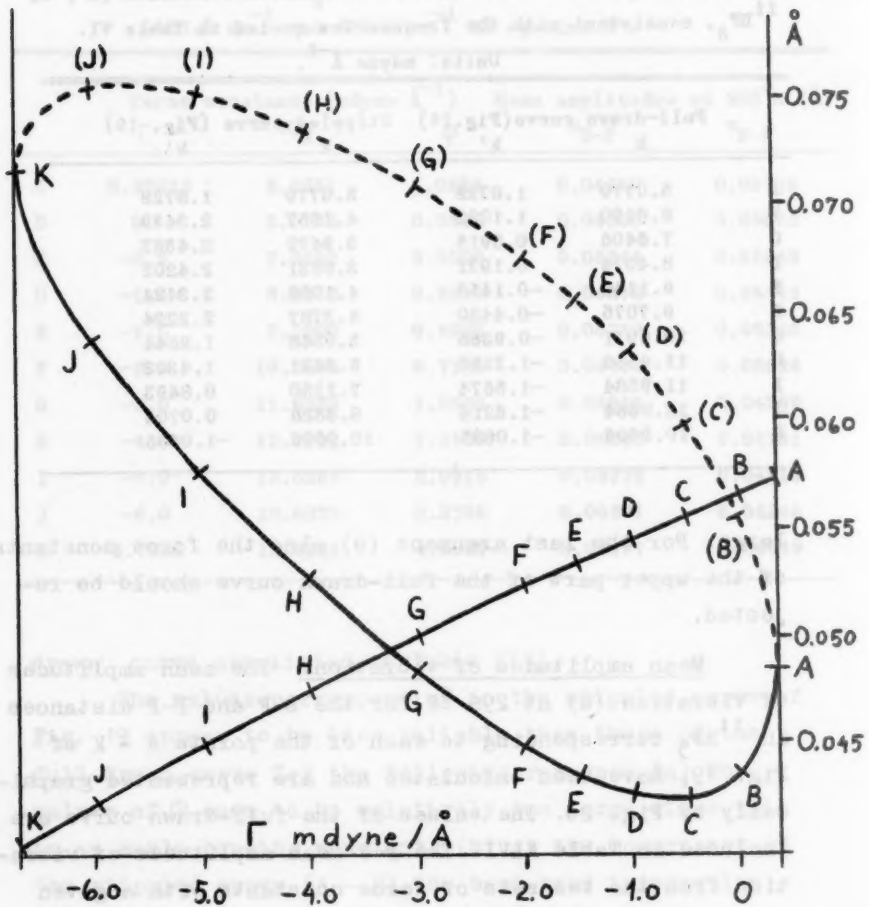
Fig.20. Mean amplitudes of vibration at 298 °K for $^{11}BF_3$, consistent with the three proper frequencies quoted in Table VI.

6.2.

on the stippled curve, and in the whole of the left hand
part of the diagram. Hence the values on those parts of
the curves should be rejected, in perfect agreement
with the discussion of the force constant values above.

$\underline{\text{Discussion.}}$ If one of the mean amplitudes of
vibration of the molecule here considered is known, in
addition to the normal frequencies, two alternative
sets of force constants may be selected. With the pre-
cise knowledge of both of the mean amplitudes of vibra-
tion, the values being consistent with the curves of
Fig. 20, and the normal frequencies, the proper set of
force constants could be determined without ambiguity.

In the following discussion it will be assumed
that the actual values are found within the range A to
G of the full-drawn curves of Figs. 19 and 20. This
corresponds to $-3.0 \leq \Gamma \leq 0.35953$ in mdyne $Å^{-1}$. Both
of the mean amplitudes of vibration vary by ± 6 to 7
percent within this range. The influence on the force
constants K_2 and φ of this variation is found to be
± 57 and ± 36 percent, respectively. Hence the rough
conclusion may be drawn, that an uncertainty of at most
1 or 2 percent in the mean amplitudes of vibration is
required, if they are supposed to be of some value in
the force constant determination. The required accuracy
for the B-F mean amplitudes of vibration depends some-
what on its magnitude, and is greatest at the minimum
of the curve of Fig. 20, i.e. in the vicinity of the
point C.

The mean amplitudes of vibration of boron tri-
fluoride have not been investigated by electron-diffraction
so far.

6.2.

<u>Compatibility with the observed frequencies for</u>
<u>$^{10}BF_3$.</u> The computed force constants (Table XLV) were
applied for calculating the vibrational frequencies of
the species E' (ν_3 and ν_4) for $^{10}BF_3$ according to
equations (2.52). The results are listed in Table
XLVIII. It is seen that the whole range of real force
constants yields comparatively acceptable results, the
deviations from the observed frequencies (see Table VI)
amounting to about ± 3.5 percent. It should be noted
that the greatest discrepancies occur at the least
reliable range of the force constants.

In the previous calculations (chapter 2), the
experimental value of ν_3 for $^{10}BF_3$ was used, together
with the frequencies for $^{11}BF_3$. The results from that
calculations correspond to a point on the curves of
Figs. 19 and 20 between C and D.

Table XLVIII. Calculated frequencies of species E' for $^{10}BF_3$,
and their deviations from observed values.

	$\nu_3/c(cm^{-1})$	Dev.(%)	$\nu_4/c(cm^{-1})$	Dev.(%)
A	1512.9	+0.54	480.4	−0.33
B	1510.0	+0.35	481.3	−0.15
C	1505.8	+0.07	482.6	+0.12
D	1501.7	−0.20	484.0	+0.41
E	1497.6	−0.47	485.3	+0.68
F	1493.4	−0.75	486.7	+0.98
G	1485.1	−1.30	489.4	+1.54
H	1476.7	−1.86	492.2	+2.12
I	1468.2	−2.43	495.0	+2.70
J	1459.6	−3.00	497.9	+3.30
K	1453.5	−3.40	500.0	+3.73

6.3.

6.3. Treatment of the germanium tetrachloride molecule

A theoretical treatment of the tetrahedral XY_4 molecular model is given in section 4.5. In species F_2 of this model, there are two normal frequencies and three force constants, viz. K_3, ϕ_4 and Γ. Here the germanium tetrachloride molecule will be treated, and the connection between the force constants of species F_2 and the mean amplitudes of vibration will be studied. Two different methods will be applied, namely Morino's simple approximation method, and the secular equation method described in chapter 4.

Application of Morino's simple approximation. All of the vibrational frequencies of germanium tetrachloride (see Table XXXII) are far below 1200 cm^{-1}. Hence the application of Morino's approximation (5.3) is justified in this case. According to this approximation it is found, for the mean-square amplitudes of vibration for the two types of interatomic distances in XY_4 [see equation (5.4) and Table XXXVIII], that:

$$u_{X-Y}^2 = \frac{h^2(\mu_X + \mu_Y)}{64\pi^2 kT} + \frac{kT}{4K_1} + \frac{3kT\phi_4}{4(K_3\phi_4 - \Gamma^2)} , \qquad (6.1)$$

$$u_{Y\cdots Y}^2 = \frac{h^2\mu_Y}{32\pi^2 kT} + \frac{2kT}{3K_1} + \frac{kT}{9\phi_2}$$

$$+ \frac{kT(K_3 + 4\phi_4 - 4\Gamma)}{6(K_3\phi_4 - \Gamma^2)} . \qquad (6.2)$$

The notation is the same as that previously used. A further simplification may be introduced by [see (4.50)]

6.3.

$$K_3 \phi_4 - \Gamma^2 = \frac{\lambda_3 \lambda_4}{2(4\mu_X + \mu_Y)\mu_Y} . \tag{6.3}$$

With the numerical values for germanium tetrachloride one has at 298 °K:

$$u_{Ge-Cl}^2 = 0.00042698 + 0.0069999\, \phi_4 , \tag{6.4}$$

$$u_{Cl\cdots Cl}^2 = 0.0051782 + 0.0015555(K_3 + 4\phi_4 - 4\Gamma). \tag{6.5}$$
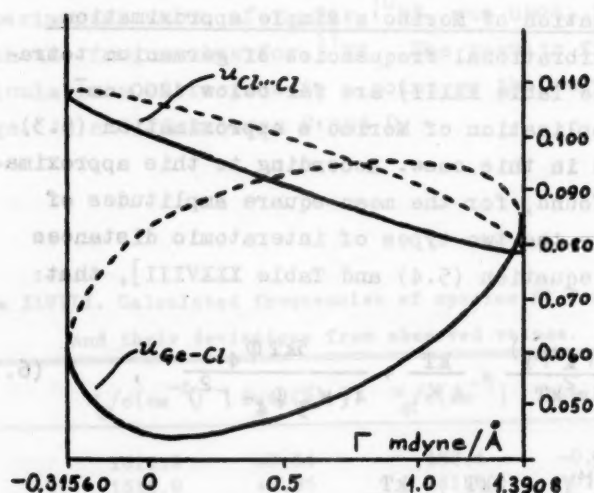
Fig. 21. Mean amplitudes of vibration at 298 °K for GeCl₄ according to Morino's simple approximation, and consistent with the observed frequencies.

6.3.
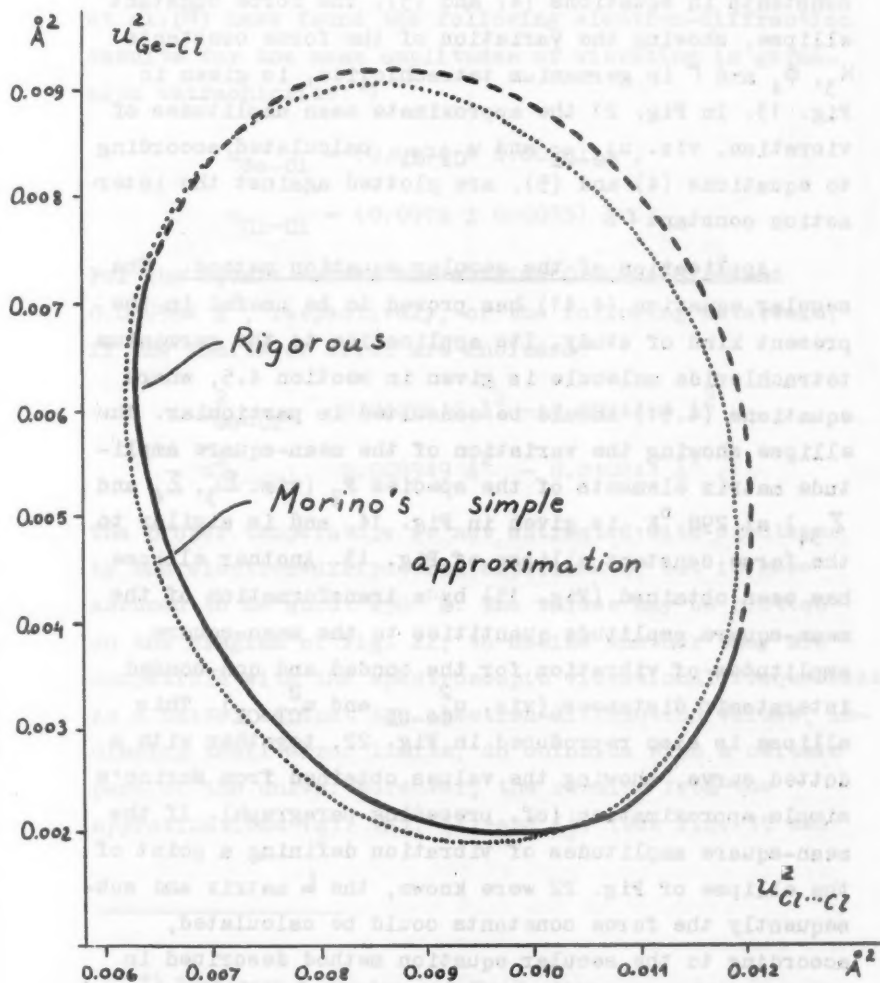
Fig. 22. Mean—square amplitudes of vibration at 298 °K for
germanium tetrachloride, consistent with the observed
frequencies. (See also Fig. 15.)

6.3.

To obtain the mean-square amplitudes of vibration in Å^2 units, the units mdyne Å^{-1} should be used for the force constants in equations (4) and (5). The force constant ellipse, showing the variation of the force constants K_3, ϕ_4 and Γ in germanium tetrachloride, is given in Fig. 13. In Fig. 21 the approximate mean amplitudes of vibration, viz. u_{Ge-Cl} and $u_{Cl\cdots Cl}$, calculated according to equations (4) and (5), are plotted against the interaction constant Γ.

Application of the secular equation method. The secular equation (4.11) has proved to be useful in the present kind of study. Its application to the germanium tetrachloride molecule is given in section 4.5, where equations (4.51) should be consulted in particular. The ellipse showing the variation of the mean-square amplitude matrix elements of the species F_2 (viz. Σ_3, Σ_4 and Σ_{34}) at 298 °K, is given in Fig. 14, and is similar to the force constant ellipse of Fig. 13. Another ellipse has been obtained (Fig. 15) by a transformation of the mean-square amplitude quantities to the mean-square amplitudes of vibration for the bonded and non-bonded interatomic distances (viz. u^2_{Ge-Cl} and $u^2_{Cl\cdots Cl}$). This ellipse is also reproduced in Fig. 22, together with a dotted curve, showing the values obtained from Morino's simple approximation (cf. preceding paragraph). If the mean-square amplitudes of vibration defining a point of the ellipse of Fig. 22 were known, the L matrix and subsequently the force constants could be calculated, according to the secular equation method described in chapter 4. It is emphasized that the new secular equation(4.11) makes it possible to perform these calculations without any graphical interpolation.

In the following paragraph, the calculations

6.3.

outlined above will be performed with the use of elec-
tron-diffraction values of mean amplitudes of vibration.

    <u>Inclusion of electron-diffraction values.</u> Morino
et al.([99]) have found the following electron-diffraction
results for the mean amplitudes of vibration in germa-
nium tetrachloride: *)

$$u_{Ge-Cl} = (0.0474 \pm 0.0020) \text{ Å} \ ,$$

$$u_{Cl\cdots Cl} = (0.0979 \pm 0.0033) \text{ Å} \ .$$

For the square values one obtains 0.0022468 Å^2 and
0.009584 Å^2, respectively, or the following intervals,
if the limits of error are included:

$$u_{Ge-Cl}^2: \quad 0.0020612 \text{ Å}^2 - 0.0024404 \text{ Å}^2 \ ,$$

$$u_{Cl\cdots Cl}^2: \quad 0.008949 \text{ Å}^2 - 0.010241 \text{ Å}^2 \ .$$

The proper temperature is not estimated with exactness
by the electron-diffraction experiments, but is here
assumed to be about 298 $^{\circ}$K. The values may be plotted
on the diagram of Fig. 22, to decide whether they are
compatible with the spectroscopic vibrational frequencies.
As a matter of fact the electron-diffraction values, in-
cluding their error limits, do coincide with a certain
part of the curve. Moreover, the results from the
approximations (g), (h), (i) and (j) (see Fig. 15 and

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*) Professor Y. Morino and Mr. T. Iijima have kindly
    supplied these results before publication to the
    author, who wishes to express his gratitude.

6.3.
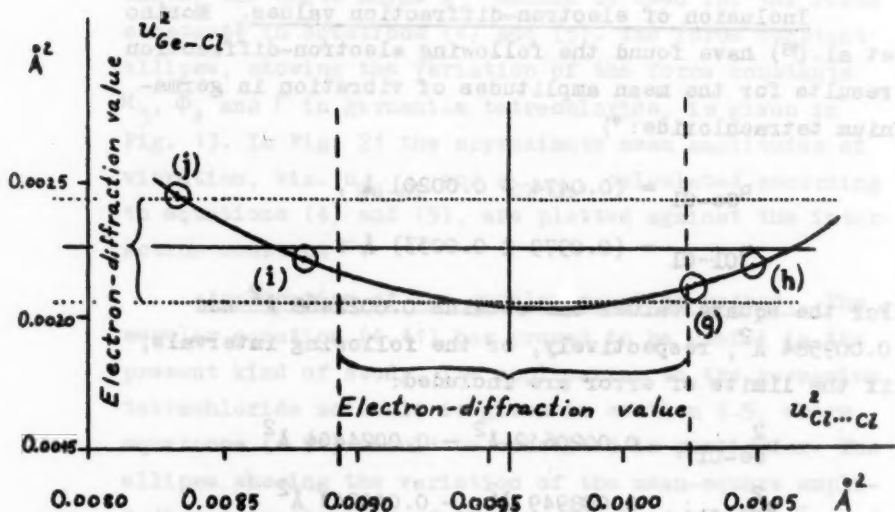
Fig. 23. Part of the mean—square amplitude ellipse (Fig.15) for germanium tetrachloride at 298 °K, including the electron-diffraction values.

the connected text) are in the same vicinity. An enlarged reproduction of the actual part of the diagram here considered, is given in Fig. 23. It is seen that the experimentally determined interval for $u^2_{Cl\cdots Cl}$ defines a narrower part of the curve that that for u^2_{Ge-Cl}, in spite of the fact that the limits of error are greater for $u^2_{Cl\cdots Cl}$. Therefore it is reasonable to use the electron-diffraction value for $u^2_{Cl\cdots Cl}$ to calculate a definite set of force constants of germanium tetrachloride.

6.3.

Table XLIX. Calculated force constants and mean-square
amplitude quantities of germanium tetrachloride by inclusion
of the electron-diffraction value $u_{Cl \cdots Cl}$ = 0.0979 Å.

Force constants (mdyne Å^{-1})		Mean-square amplitudes (Å^2) T = 298 °K	
K_1	3.2912	Σ_1	0.0016116
Φ_2	0.12128	Σ_2	0.035076
K_3	2.7569	Σ_3	0.0021875
Φ_4	0.17152	Σ_4	0.027452
Γ	0.17860	Σ_{34}	−0.0021314
k_0	2.8905	σ_0	0.0020435
k_1	0.13355	σ_1	−0.0001440
f_0-f_2	0.17152	τ_0	0.025418
f_1-f_2	0.02512	τ_1	−0.0058460
$\varepsilon_0-\varepsilon_1$	0.12629	τ_2	−0.0020338
		ρ_0	−0.0060284
		ρ_1	0.0060284

In the present calculations, using $u^2_{Cl \cdots Cl}$ =
0.009584 Å^2, the corresponding mean-square amplitude
of vibration for Ge-Cl is found to have the value
0.0020435 Å^2, i.e. u_{Ge-Cl} = 0.0452 Å. This result may
be considered as compatible with the electron-diffraction
measurements, although it falls just outside the repor-
ted error limits. In Table XLIX the calculated mean-
square amplitude quantities and force constants are
listed. For the applied symbol, references are made
to section 4.5. The **L** matrix elements are found in
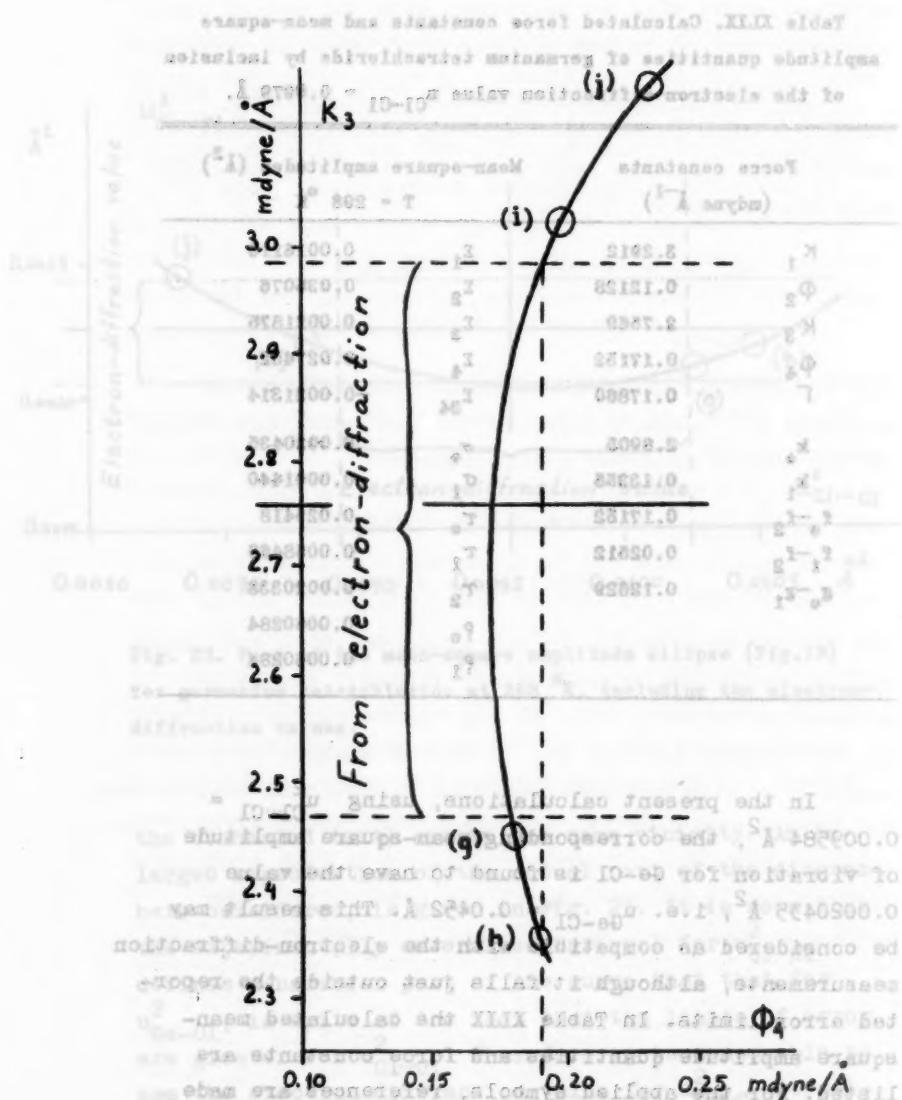
Fig. 24. Part of the force constant ellipse (Fig.13) for germanium tetrachloride, including the result from electron-diffraction.

6.3.

Table L. Tabulation of the L matrix elements for germanium
tetrachloride in (Amu)$^{-\frac{1}{2}}$ units.

GeCl$_4$	Q$_1$	Q$_2$	Q$_3$	Q$_4$
S$_1$	0.16794			
S$_2$		0.29088		
S$_3$			0.21571	−0.00622
S$_4$			−0.16098	0.32242

Table L. A part of the ellipse for the force constants
(cf. Fig. 13) is drawn in Fig. 24, where the results
of the present calculations are indicated, together
with the whole range corresponding to the reported
limits of error for u$_{Cl\cdots Cl}$ from electron-diffraction.

7. COLLECTION OF NUMERICAL VALUES OF MEAN AMPLITUDES
OF VIBRATION AND MEAN-SQUARE AMPLITUDE MATRIX ELEMENTS

In the following tables, a collection of numerical results is presented, from the work of the present author. For details of the calculations as well as explanations of the applied symbols, references are made to the original publications.

Some approximate calculations using the four-constant approximation for the hyperbolic cotangent, are not included here. For this subject, references are made to chapter 5 and one of the publications [44].

Table LI. Mean amplitudes of vibration, calculated from spectroscopic data, by the rigorous method.

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
$^{12}CO_2$	C–0	0.03457	0.03459	[11]
	0··0	0.03945	0.03951	
$^{13}CO_2$	C–0	0.03424	0.03425	[11]
	0··0	0.03945	0.03951	
$^{14}CO_2$	C–0	0.03394	0.03396	[11]
	0··0	0.03945	0.03951	
CS_2	C–S	0.0383	0.0387	[11]
	S··S	0.0396	0.0412	

7.

Table LI (Continued).

Molecule	Distance	Mean amplitude in Å		Reference
		$T = 0$	298 °K	
CSe_2	C—Se	0.0381	0.0397	[11]
	Se—Se	0.0341	0.0404	
COS	C—O	0.0349	0.0349	[11]
	C—S	0.0383	0.0387	
	O—S	0.0405	0.0410	
COSe	C—O	0.0349	0.0350	[11]
	C—Se	0.0387	0.0399	
	O—Se	0.0398	0.0414	
CSSe	C—S	0.0384	0.0389	[11]
	C—Se	0.0384	0.0397	
	S—Se	0.0376	0.0410	
CSTe	C—S	0.0390	0.0396	[11]
	C—Te	0.0395	0.0418	
	S—Te	0.0381	0.0433	
$^{14}NO_2$	N—O	0.0382	0.0382	[10], [*]
	O—O	0.0459	0.0469	
$^{15}NO_2$	N—O	0.0378	0.0379	[10], [*]
	O—O	0.0461	0.0469	
P_4	P—P	0.0464	0.0511	[29]
$^{11}BF_3$	B—F	0.0424	0.0425	[28], [*]
	F—F	0.0517	0.0552	
$^{11}BCl_3$	B—Cl	0.0478	0.0491	[28]
	Cl—Cl	0.0536	0.0689	
$^{11}BBr_3$	B—Br	0.0479	0.0506	[28]
	Br—Br	0.0461	0.0726	

7.

Table LI (Continued).

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
$^{11}BI_3$	B—I	0.0508	0.0570	[25]
	I···I	0.0449	0.0848	
NH_3	N—H		0.0727	[44]
	H—H		0.1236	
ND_3	N—D		0.0618	[44]
	D—D		0.1040	
$GeCl_4$	Ge—Cl	0.0403	0.0458	[*][MVP-ℓ]
	Cl—Cl	0.0651	0.1014	
CH_3Cl	C—H	0.0761	0.0761	[43]
	C—Cl	0.0472	0.0485	
	H—H	0.1285	0.1286	
	H—Cl	0.1246	0.1252	
CD_3Cl	C—D	0.0652	0.0652	[43]
	C—Cl	0.0489	0.0503	
	D—D	0.1090	0.1094	
	D—Cl	0.0980	0.0997	
CH_3Br	C—H	0.0759	0.0759	[43]
	C—Br	0.0494	0.0519	
	H—H	0.1301	0.1302	
	H—Br	0.1193	0.1204	
CD_3Br	C—D	0.0651	0.0651	[43]
	C—Br	0.0489	0.0515	
	D—D	0.1100	0.1106	
	D—Br	0.1013	0.1039	

7.

Table LI (Continued).

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
CH_3I	C—H	0.0758	0.0758	[43]
	C—I	0.0511	0.0549	
	H—H	0.1309	0.1311	
	H—I	0.1229	0.1247	
CD_3I	C—D	0.0649	0.0649	[43]
	C—I	0.0503	0.0543	
	D—D	0.1107	0.1113	
	D—I	0.1043	0.1081	
C_3H_4	C—H	0.0772	0.0772	[33]
(Allene)	C—H	0.1010	0.1015	
	C—H	0.1138	0.1144	
	C—C	0.0400	0.0401	
	C—C	0.0450	0.0451	
	H—H	0.1272	0.1273	
	H—H	0.1642	0.1716	
C_3D_4	C—D	0.0656	0.0656	[33]
(Allene—d_4)	C—D	0.0877	0.0888	
	C—D	0.0989	0.1005	
	C—C	0.0399	0.0399	
	C—C	0.0450	0.0451	
	D—D	0.1075	0.1080	
	D—D	0.1388	0.1506	
C_3H_6	C—H	0.0750	0.0750	[*]
(Cyclo-	C—H	0.1082	0.1090	
propane)	C—C	0.0510	0.0514	
	$H_1 \cdots H_1'$	0.1180	0.1181	

7.

Table LI (Continued).

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
(C_3H_6)	$H_2 \cdots H_3$	0.1758	0.1783	[2]
	$H_2 \cdots H_3^!$	0.1316	0.1320	
C_3D_6	C–D	0.0643	0.0643	[2]
(Cyclo-	C–D	0.0944	0.0964	
propane-d_6)	O–C	0.0506	0.0511	
	$D_1 \cdots D_1^!$	0.1007	0.1010	
	$D_2 \cdots D_3$	0.1484	0.1552	
	$D_2 \cdots D_3^!$	0.1137	0.1148	
C_6H_6	$C_1 \cdots H_1$	0.0771	0.0771	[19], [15]
(Benzene)	$C_1 \cdots H_2$	0.1000	0.1004	
	$C_1 \cdots H_3$	0.0952	0.0960	
	$C_1 \cdots H_4$	0.0928	0.0942	
	$C_1 - C_2$	0.0457	0.0459	[19]
	$C_1 \cdots C_3$	0.0534	0.0547	
	$C_1 \cdots C_4$	0.0576	0.0597	
	$H_1 \cdots H_2$	0.1556	0.1561	
	$H_1 \cdots H_3$	0.1313	0.1321	
	$H_1 \cdots H_4$	0.1179	0.1191	
C_6D_6	$C_1 - D_1$	0.0660	0.0660	[17]
(Benzene-d_6)	$C_1 \cdots D_2$	0.0889	0.0898	
	$C_1 \cdots D_3$	0.0835	0.0848	
	$C_1 \cdots D_4$	0.0821	0.0839	
	$C_1 - C_2$	0.0455	0.0457	
	$C_1 \cdots C_3$	0.0529	0.0543	
	$C_1 \cdots C_4$	0.0570	0.0593	

7.

Table LI (Continued).

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
(C_6D_6)	D_1-D_2	0.1277	0.1296	[27]
	$D_1\cdots D_3$	0.1095	0.1112	
	D_1-D_4	0.1012	0.1028	

(*) Present thesis.

Table LII. Mean amplitudes of vibration, calculated from spectroscopic data, assuming simplified molecular models.

Molecule	Distance	Mean amplitude in Å		Reference
		T = 0	298 °K	
C_3H_4	C–C	0.0398		[34]
(Allene)	C··C	0.0473		
C_3D_4	C–C	0.0401		[34]
(Allene-d_4)	C··C	0.0491		
C_3H_6	C–H	0.0720		(*)
(Cyclo-	C–C	0.0489		[16]
propane)		0.0464	0.0467	(*)
C_3D_6	C–D	0.0606		(*)
(Cyclo-propane-d_6)	C–C	0.0476	0.0481	
C_6H_6	C_1-C_2	0.0430	0.0431	[35]
(Benzene)	$C_1\cdots C_3$	0.0523	0.0532	
	$C_1\cdots C_4$	0.0580	0.0597	

7.

Table LII (Continued).

Molecule	Distance	Mean amplitude in λ		Reference
		$T = 0$	$298\ ^\circ K$	
C_6D_6	C_1-C_2	0.0424	0.0425	[35]
(Benzene-d_6)	$C_1\cdots C_3$	0.0517	0.0528	
	$C_1\cdots C_4$	0.0573	0.0593	

(*) Present thesis.

Table LIII. Tabulation of mean-square amplitude matrix elements at 298 $^\circ K$, calculated from spectroscopic data.

Molecule	Species	Mean-square amplitude in λ^2 298 $^\circ K$	Reference
$^{16}O_2$		0.0013351	(*)
$^{32}S_2$		0.0015435	(*)
$^{80}Se_2$		0.0014588	(*)
$^{12}CO_2$	A_{1g}	0.0007804	(*)
	A_{2u}	0.0016122	
$^{13}CO_2$	A_{1g}	0.0007804	(*)
	A_{2u}	0.0015663	
$^{14}CO_2$	A_{1g}	0.0007804	(*)
	A_{2u}	0.0015261	
CS_2	A_{1g}	0.0008471	(*)
	A_{2u}	0.0021507	
CSe_2	A_{1g}	0.0008063	(*)
	A_{2u}	0.0023149	

7.

Table LIII (Continued).

Molecule	Species	Mean-square amplitude in $\AA^2$ 298 °K		Reference
$^{14}NO_2$	A_1	Σ_1	0.0010561	(*), (30)
		Σ_2	0.0076139	
		Σ_{12}	−0.0007355	
	B_1	Σ_3	0.0018612	
$^{15}NO_2$	A_1	Σ_1	0.0010477	(*), (30)
		Σ_2	0.0074809	
		Σ_{12}	−0.0007026	
	B_1	Σ_3	0.0018201	
P_4	A_1		0.0040174	(*), (29)
	E		0.0019687	
	F_2		0.0025611	
$^{11}BF_3$	A_1'	Σ_1	0.001027	(31)
		Σ_3	0.002195	
	E'	Σ_4	0.015103	
		Σ_{34}	0.002763	
$^{11}BCl_3$	A_1'	Σ_1	0.001242	(31)
		Σ_3	0.002999	
	E'	Σ_4	0.024279	
		Σ_{34}	0.003521	
$^{11}BBr_3$	A_1'	Σ_1	0.001297	(31)
		Σ_3	0.003190	
	E'	Σ_4	0.033563	
		Σ_{34}	0.005572	

7.

Table LIII (Continued).

Molecule	Species		Mean-square amplitude in $\AA^2$	Reference
			298 °K	
$^{11}BI_3$	A_1'	Σ_1	0.001631	(*)
		Σ_3	0.004051	
	E'	Σ_4	0.032465	
		Σ_{34}	0.003261	
$GeCl_4$	A_1	Σ_1	0.0016116	(*)[MVP-ℓ]
	E	Σ_2	0.035076	
		Σ_3	0.0022655	
	F_2	Σ_4	0.024594	
		Σ_{34}	−0.0004577	

(*) Present thesis.

The principal scope of the present work is a spectroscopic study of mean amplitudes of vibration, under the approximate assumption of small harmonic oscillations. If the instantaneous intramolecular distance between an arbitrary pair of atoms in a molecule is denoted by R, and the equilibrium distance by R_e, then the corresponding mean amplitude of vibration (u) is defined by

$$u = \left[\overline{(R - R_e)^2} \right]^{\frac{1}{2}}.$$

Chapter 1. A review is given of the work done in the field of mean amplitudes of vibration. The principles of determining mean amplitudes of vibration both from electron-diffraction and from spectroscopic data, are surveyed. Comprehensive tables of references to the studies of individual molecules are presented, as well as selected numerical values of mean amplitudes of vibration from the literature.

Chapter 2. This chapter is initiated by the author's adaptation of the L matrix method of calculating mean amplitudes of vibration, which was originally developed by Morino et al. By this method the complete potential energy matrix (F) must be established, to get the K_{1k} coefficients of the expression

$$r_1 = \sum_k K_{1k} Q_k,$$

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where r_i is an interatomic distance displacement coordinate, and Q_k represents the normal coordinates. Then the mean-square amplitude of vibration (u^2) is given by

$$u^2 = \overline{r_i^2} = \sum_k K_{ik}^2 (h/8\pi^2 \nu_k) \coth(h\beta\nu_k/2) \; ; \quad \beta = 1/kT \; .$$

The expressions of mean-square amplitudes of vibration are given for some simple molecular models, viz. diatomic, linear symmetrical XY_2, regular trigonal X_3, plane square X_4, and the tetrahedral X_4 molecular models.

Next the present method is applied to the plane symmetrical XY_3 molecular model, and the calculations for boron trifluoride are reported.

Finally the cyclopropane molecular model is treated, and the numerical computations for C_3H_6 and C_3D_6 are reported. In this case one has twenty-one internal coordinates, twenty-seven harmonic force constants, and fourteen normal frequencies. The normal frequencies were obtained from observed fundamentals taken from the literature and corrected for anharmonicity. Some approximations had to be introduced in order to decrease the number of unknowns in the force field determination, although the normal frequencies from both C_3H_6 and C_3D_6 were utilized. As the final result, the six types of mean amplitudes of vibration for cyclopropane and cyclopropane-d_6 at absolute zero and 298 $^\circ$K, are tabulated.

Chapter 3. It is pointed out that in many cases the rigorous computations of mean amplitudes of vibration may be greatly facilitated by assuming simplified molecular models. Still valuable results may be obtained if not a too great accuracy is claimed. These aspects are

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illustrated by an application to the C-H (C-D) and C-C
mean amplitudes of vibration in the cyclopropane mole-
cules, the results being compared with those from the
rigorous calculations.

Chapter 4. The mean-square amplitude matrix (Σ)
is defined as

$$\Sigma = S\widetilde{S},$$

where S denotes a set of internal coordinates represen-
ted by a column matrix. The mean-square amplitudes of
vibration, viz. $\overline{\delta_i^2}$, appear along the main diagonal of
this matrix, the off-diagonal elements ($\Sigma_{ij} = \overline{\delta_i \delta_j}$)
representing some quantities of a new type, referred to
as the "interaction mean-square amplitudes". Two novel
secular equations containing the Σ matrix are presented,
viz.

$$|\Sigma G^{-1} - \Delta E| = 0 ,$$

and

$$|\Sigma F - \lambda \Delta E| = 0 .$$

The characteristic values are

$$\Delta_k = (h/8\pi^2 \nu_k)\coth(h\beta\nu_k/2)$$

and

$$\lambda_k \Delta_k = \tfrac{1}{2}h\nu_k \coth(h\beta\nu_k/2) ,$$

respectively. The secular equations have certain advan-
tages in solving the vibrational problems, and, depending
on the special conditions, the new secular equation
methods supplement Morino's L matrix method. In particular,

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the first one of the secular equations here reported is applicable for the calculation of force constants from known mean-square amplitudes of vibration. An isotope rule for the mean-square amplitude matrices is also given.

A treatment of the simple molecular models specified under the summary of chapter 2, is present, including some numerical examples.

A theoretical study of the mean-square amplitude matrix for the bent symmetrical XY_2 molecular model is reported, as well as an application to nitrogen dioxide. A "mean-square amplitude ellipse" is worth while mentioning, showing the variation of the three mean-square amplitude matrix elements of the species A_1, possessing real values and being consistent with the two normal frequencies of this species. This graph is similar to the familiar force constant ellipse, which in the case of nitrogen dioxide is included in the present chapter.

The final subject of this chapter is an extensive treatment of the tetrahedral XY_4 molecular model, with the application to germanium tetrachloride. For this molecule a number of tentative approximations are used and discussed, such as the so-called "valence force mean-square amplitude" and "central force mean-square amplitude" approximations. These approximations are analogous to the well-known valence force field and central force field, which also are included in the present computations. The force constant and mean-square amplitude ellipses are given also in this case.

Chapter 5. Morino et al. have evaluated an approximate method for computing mean amplitudes of vibration, based on the approximation

$$\coth t = \frac{1}{t} + \frac{t}{4} \, ,$$

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applied to $t = h\beta\nu_k/2$ ($\beta = 1/kT$). By this method the computation of the L matrix is avoided, but the F matrix is still required. In the present chapter an extension of this method is given, assuming

$$\coth t = -\theta_{-3}t^{-3} + \theta_{-1}t^{-1} + \theta_1 t - \theta_3 t^3 .$$

Numerical values for the constants θ are given, and have been adjusted to selected ranges of normal frequencies (ν_k) by a least-squares method. It is pointed out that the approximate methods may be applied for computing the whole mean-square amplitude matrix, and not only the mean-square amplitudes of vibration.

The expressions of the approximate mean-square amplitudes of vibration according to the present method are given for the linear symmetrical XY_2 molecular model, tetrahedral X_4, linear YXZ, linear symmetrical X_2Y_2, plane symmetrical XY_3, and the tetrahedral XY_4 molecular models. Numerical examples for $^{11}BF_3$ and $GeCl_4$ are included.

Next the plane symmetrical XY_2Z molecular model is treated theoretically, and the calculations of mean amplitudes of vibration for formaldehyde are reported.

As a conclusion it is stated that the four-constant hyperbolic cotangent approximation leads to fairly good results (about 0.5 percent error in the mean amplitudes of vibration), but the computations are not always simple, so that the L matrix method in many cases may be preferred.

Chapter 6. This chapter is concerned with the problem of using mean amplitudes of vibration obtained from electron-diffraction, in addition to the normal frequencies, in the detection of the force field of a

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polyatomic molecule. A special definition of a vibrational
constant is used to classify the various cases of the
problem.

In the case of $^{11}BF_3$, there exist two normal frequen-
cies and three harmonic force constants belonging to the
species E'. To calculate the complete harmonic force field,
the additional information of either the mean amplitudes
of vibration, or a normal frequency for an isotopic mole-
cule, say $^{10}BF_3$, may be utilized. These aspects are dis-
cussed in the present chapter, and the rough conclusion
is drawn, that an uncertainty of not more than 1 or 2
percent in the mean amplitudes of vibration is required,
if they are expected to be of some value in the force
constant determination.

A similar situation to that of the E' species in
the above case, occurs in the species F_2 of tetrahedral
XY_4 molecules. As an illustration, the germanium tetra-
chloride molecule is treated, and the usefullness of the
new secular equation method is demonstrated. In a diagram
the ellipse of the mean-square amplitudes of vibration,
consistent with the observed vibrational frequencies, is
drawn together with the curve obtained from Morino's
simple approximation. This approximation proves to be
very good in the present case. The electron-diffraction
values of mean amplitudes of vibration of $GeCl_4$, produced
by Morino et al., appeared to be compatible with the mean-
square amplitude ellipse, within their limits of error.
In the present calculations the value for the non-bonded
atom pair, viz. Cl...Cl, was used for calculating the complete
force constant matrix of the F_2 species for the molecule
under consideration.

Chapter 7. Here a collection of numerical results
from the present author's calculations is given. Mean

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amplitudes of vibration and mean-square amplitude elements are tabulated.

REFERENCES

1. AINSWORTH,J. and KARLE,J., J.Chem.Phys. 20, 425 (1952).

2. AIMENNINGEN,A. and BASTIANSEN,O., Kgl. Norske Videnskab. Selskabs Skrifter, No.4 (1958).

3. AIMENNINGEN,A. and BASTIANSEN,O., Research Correspondence 9, 35 (1956).

4. AIMENNINGEN,A., BASTIANSEN,O. and FERNHOLT,L., Kgl.Norske Videnskab.Selskabs Skrifter,No.3 (1958).

5. AIMENNINGEN,A., BASTIANSEN,O. and MUNTHE-KAAS,T., Acta Chem.Scand. 10, 261 (1956).

6. AIMENNINGEN,A., BASTIANSEN,O. and TRÆTTEBERG,M., Acta Chem.Scand. 13, 1699 (1959).

7. AIMENNINGEN,A., BASTIANSEN,O. and TRÆTTEBERG,M., J.Chem.Phys. (In press).

8. ARAKAWA,E.T. and NIELSEN,A.H., J.Mol.Spectroscopy 2, 413 (1958).

9. BAKER,A.W. and LORD,R.C., J.Chem.Phys. 23, 1636 (1955).

10. BAKKEN,J., Acta Chem.Scand. 12, 594 (1958).

11. BARTELL,L.S., J.Chem.Phys. 23, 1219 (1955).

12. BARTELL,L.S. and BONHAM,R.A., J.Chem.Phys. 31, 400 (1959).

13. BARTELL,L.S. and BROCKWAY,L.O., J.Chem.Phys. 23, 1860 (1955).

14. BARTELL,L.S. and BROCKWAY,L.O., Nature 171, 978 (1953).

15. BARTELL,L.S., BROCKWAY,L.O. and SCHWENDEMAN,R.H., J.Chem.Phys. 23, 1854 (1955).

16. BARTELL,L.S. and HIRST,R.C., J.Chem.Phys. 31, 449 (1959).

17. BASTIANSEN,O., 8.Nordiske Kjemikermøte, Oslo (1953).

18. BASTIANSEN,O. and CYVIN,S.J., Acta Chem.Scand. 11, 1789 (1957).

References

19. BASTIANSEN,O. and CYVIN,S.J., Nature 180, 980 (1957).

20. BASTIANSEN,O., HEDBERG,L. and HEDBERG,K., J.Chem. Phys. 27, 1311 (1957).

21. BIRD,G.R., J.Chem.Phys. 25, 1040 (1956).

22. BLOCH,F., Z.Physik 74, 295 (1932).

23. BOND,A.C. and BROCKWAY,L.O., J.Am.Chem.Soo. 76, 3312 (1954).

24. BONHAM,R.A. and BARTELL,L.S., J.Am.Chem.Soo. 81, 3491 (1959).

25. CYVIN,S.J., Acta Chem.Scand. 11, 1499 (1957).

26. CYVIN,S.J., Acta Chem.Scand. 12, 1697 (1958).

27. CYVIN,S.J., Acta Chem.Scand. 12, 1697 (1958).

28. CYVIN,S.J., Acta Chem.Scand. 13, 334 (1959).

29. CYVIN,S.J., Acta Chem.Scand. 13, 1397 (1959).

30. CYVIN,S.J., Acta Chem.Scand. 13, 1400 (1959).

31. CYVIN,S.J., Acta Chem.Scand. 13, 1809 (1959).

32. CYVIN,S.J., Acta Chem.Scand. 13, 2135 (1959).

33. CYVIN,S.J., J.Chem.Phys. 29, 583 (1958).

34. CYVIN,S.J., J.Chem.Phys. 30, 337 (1959).

35. CYVIN,S.J., J.Mol.Spectroscopy 3, 467 (1959).

36. CYVIN,S.J., Kgl. Norske Videnskab. Selskabs Skrifter, No. 2 (1959).

37. CYVIN,S.J., Spectrochim.Acta, 56 (1959).

38. CYVIN,S.J., Spectrochim.Acta, 341 (1959).

39. CYVIN,S.J., Spectrochim.Acta, 828 (1959).

40. CYVIN,S.J., Spectrochim.Acta, 835 (1959).

41. CYVIN,S.J., Spectrochim.Acta, 958 (1959).

42. CYVIN,S.J., Tidsskr.Kjemi,Bergv.,Met. 19, 83 (1959).

43. CYVIN,S.J., Z.physik.Chem. Neue Folge (In press).

44. CYVIN,S.J. and BAKKEN,J., Acta Chem.Scand. 12, 1759 (1958).

45. DARLING,B.T. and DENNISON,D.M., Phys.Rev. 57, 128 (1940).

References

46. DEBYE,P., J.Chem.Phys. $\underline{9}$, 55 (1941).

47. DECIUS,J.C., J.Chem.Phys. $\underline{16}$, 1025 (1948).

48. DECIUS,J.C., J.Chem.Phys. $\underline{21}$, 1121 (1953).

49. DENNISON, D.M., Revs.Modern Phys. $\underline{3}$, 280 (1931).

50. DENNISON, D.M., Revs.Modern Phys. $\underline{12}$, 175 (1940).

51. DUCHESNE,J. and BURNELLE,L., J.Chem.Phys. $\underline{19}$, 1191 (1951).

52. DUCHESNE,J. and NIELSEN,A.H., J.Chem.Phys. $\underline{20}$, 1968 (1958).

53. ELIASHEVICH,M.A., Compte rendus U.R.S.S. $\underline{28}$, 604 (1940).

54. GLAUBER,R. and SCHOMAKER,V., Phys.Rev. $\underline{89}$, 667 (1953).

55. GLOCKLER,G., Revs.Modern Phys. $\underline{15}$, 111 (1943).

56. GLOCKLER,G. and TUNG,J., J.Chem.Phys. $\underline{13}$, 388 (1945).

57. GÜNTHARD,H.H., LORD,R.C. and McCUBBIN,T.K.Jr., J.Chem.Phys. $\underline{25}$, 768 (1956).

58. HANSEN,G.E. and DENNISON,D.M., J.Chem.Phys. $\underline{20}$, 313 (1952).

59. HARVEY,R.B. and BAUER,S.H., J.Am.Chem.Soc. $\underline{75}$, 2840 (1953).

60. HEATH,D.F. and LINNETT,J.W., Trans.Faraday Soc. $\underline{44}$, 556 (1948).

61. HEATH,D.F. and LINNETT,J.W., Trans.Faraday Soc. $\underline{44}$, 561 (1948).

62. HEATH,D.F. and LINNETT,J.W., Trans.Faraday Soc. $\underline{44}$, 873 (1948).

63. HEATH,D.F. and LINNETT,J.W., Trans.Faraday Soc. $\underline{44}$, 878 (1948).

64. HERZBERG,G., Molecular Spectra and Molecular Structure. Vol.II. Infrared and Raman Spectra of Polyatomic Molecules, D.van Nostrand, New York 1945.

65. HESLOP,W.R. and LINNETT,J.W., Trans.Faraday Soc. $\underline{49}$, 1262 (1953).

References

66. HIROTA,E., Bull.Chem.Soc.Japan 31, 130 (1958).

67. IWASAKI,M., Bull.Chem.Soc.Japan 31, 1071 (1958).

68. IWASAKI,M., Bull.Chem.Soc.Japan 32, 194 (1959).

69. IWASAKI,M., NAGASE,S. and KOJIMA,R., Bull.Chem.
    Soc.Japan 30, 230 (1957).

70. JAMES,R.W., Physik.Z. 33, 737 (1932).

71. KARLE,I.L., J.Chem.Phys. 20, 65 (1952).

72. KARLE,I.L., J.Chem.Phys. 23, 1739 (1955).

73. KARLE,I.L. and KARLE,J., J.Chem.Phys. 17, 1052 (1949).

74. KARLE,I.L. and KARLE,J., J.Chem.Phys. 18, 963 (1950).

75. KARLE,I.L. and KARLE,J., J.Chem.Phys. 20, 63 (1952).

76. KARLE,I.L. and KARLE,J., J.Chem.Phys. 22, 43 (1954).

77. KARLE,J. and KARLE,I.L., J.Chem.Phys. 18, 957 (1950).

78. KEIDEL,F.A. and BAUER,S.H., J.Chem.Phys. 25, 1218
    (1956).

79. KIMURA,K., J.Chem.Phys. 27, 1213 (1957).

80. KIMURA,K. and KIMURA,M., J.Chem.Phys. 25, 362 (1956).

81. KIMURA,K. and KUBO,M., J.Chem.Phys. 30, 151 (1959).

82. KIMURA,K., SUZUKI,S., KIMURA,M. and KUBO,M., Bull.
    Chem.Soc.Japan 31, 1051 (1958).

83. KIMURA,K., SUZUKI,S., KIMURA,M. and KUBO,M., J.Chem.
    Phys. 27, 320 (1957).

84. KIMURA,M., KIMURA,K., AOKI,M. and SHIBATA,S., Bull.
    Chem.Soc.Japan 29, 95 (1956).

85. KIMURA,M., KIMURA,K. and SHIBATA,S., J.Chem.Phys.
    24, 622 (1956).

86. KUCHITSU,K., Bull.Chem.Soc.Japan 30, 391 (1957).

87. KUCHITSU,K., Bull.Chem.Soc.Japan 32, 748 (1959).

88. LINDEMAN,L.P. and WILSON,M.K., J.Chem.Phys. 24,
    242 (1956).

89. LINNETT,J.W. and HEATH,D.F., Trans.Faraday Soc.
    48, 592 (1952).

References

90. MATHAI,P.M., SHEPHERD,G.G. and WELSH,H.L., Can.J. Phys. $\underline{34}$, 1448 (1956).

91. MEISTER,A.G. and CLEVELAND,F.F., Am.J.Phys. $\underline{14}$, 13 (1946).

92. MEISTER,A.G., CLEVELAND,F.F. and MURRAY,M.J., Am. J.Phys. $\underline{11}$, 239 (1943).

93. MORINO,Y., J.Chem.Phys. $\underline{18}$, 395 (1950).

94. MORINO,Y. and HIROTA,E., J.Chem.Phys. $\underline{23}$, 737 (1955).

95. MORINO,Y. and HIROTA,E., J.Chem.Phys. $\underline{28}$, 185 (1958).

96. MORINO,Y. and KUCHITSU,K., J.Chem.Phys. $\underline{28}$, 175 (1958).

97. MORINO,Y., KUCHITSU,K. and SHIMANOUCHI,T., J.Chem. Phys. $\underline{20}$, 726 (1952).

98. MORINO,Y., KUCHITSU,K., TAKAHASHI,A. and MAEDA,K., J.Chem.Phys. $\underline{21}$, 1927 (1953).

99. MORINO,Y., NAKAMURA,Y. and IIJIMA,T., J.Chem.Phys. (In press).

100. NEU,J.T. and GWINN,W.D., J.Am.Chem.Soc. $\underline{70}$, 3463 (1948).

101. PACE,E.L., J.Chem.Phys. $\underline{18}$, 881 (1950).

102. PISTORIUS,C.W.F.T., J.Chem.Phys. $\underline{27}$, 965 (1957).

103. PISTORIUS,C.W.F.T., J.Chem.Phys. $\underline{28}$, 514 (1958).

104. PISTORIUS,C.W.F.T., J.Chem.Phys. $\underline{29}$, 1174 (1958).

105. PISTORIUS,C.W.F.T., J.Chem.Phys. $\underline{29}$, 1421 (1958).

106. PISTORIUS,C.W.F.T., Z.physik.Chem. Neue Folge $\underline{16}$, 126 (1958).

107. REDLICH.O., Z.physik.Chem. $\underline{B28}$, 371 (1935).

108. REITAN,A., Acta Chem.Scand. $\underline{12}$, 131 (1958).

109. REITAN,A., Acta Chem.Scand. $\underline{12}$, 785 (1958).

110. REITAN,A., Kgl. Norske Videnskab. Selskabs Skrifter, No. 2 (1958).

111. ROSENTHAL,J.E. and MURPHY,G.M., Revs.Modern Phys. $\underline{8}$, 317 (1936).

References

112. SCHOMAKER,V. and GLAUBER,R., Nature 170, 290 (1952).

113. SHAFFER,W.H. and NEWTON,R.R., J.Chem.Phys. 10, 405 (1942).

114. SHIMANOUCHI,T., J.Chem.Phys. 17, 245 (1949).

115. SHIMANOUCHI,T., J.Chem.Phys. 17, 734 (1949).

116. SHIMANOUCHI,T., J.Chem.Phys. 17, 848 (1949).

117. SLATER,N.B., Trans.Faraday Soc. 50, 207 (1954).

118. SMITH,S. and LINNETT,J.W., Trans.Faraday Soc. 52, 891 (1956).

119. SWICK,D.A. and KARLE,I.L., J.Chem.Phys. 23, 1499 (1955).

120. SWICK,D.A., KARLE,I.L. and KARLE,J., J.Chem.Phys. 22, 1242 (1954).

121. TORKINGTON,P., J.Chem.Phys. 17, 357 (1949).

122. TORKINGTON,P., J.Chem.Phys. 17, 1026 (1949).

123. TORKINGTON,P., Proc.Phys.Soc. London A64, 32 (1951).

124. UREY,H.C. and BRADLEY,C.A., Phys.Rev. 38, 1969 (1931).

125. VENKATESWARLU,K. and SUNDARAM,S., J.Chem.Phys. 23, 2365 (1955).

126. VENKATESWARLU,K. and SUNDARAM,S., J.Chem.Phys. 23, 2368 (1955).

127. VENKATESWARLU,K. and SUNDARAM,S., J.Chim.Phys. France, 202 (1957).

128. VIERVOLL,H., Acta Chem.Scand. 1, 120 (1947).

129. VOLKENSTEIN,M.V., ELIASHEVICH,M.A. and STEPANOV, B.I., Kolebanyia molekul (Vibrations of molecules), Vol.I., GITTL, Moscow 1949.

130. WENTINK,T.Jr., J.Chem.Phys. 30, 105 (1959).

131. WENTINK,T.Jr. and TIENSUU,V.H., J.Chem.Phys. 28, 826 (1958).

132. WILSON,E.B.Jr., J.Chem.Phys. 7, 1047 (1939).

133. WILSON,E.B.Jr., J.Chem.Phys. 9, 76 (1941).

References

134. WILSON,E.B.Jr., J.Chem.Phys. 15, 736 (1947).

135. WILSON,E.B.Jr. and CRAWFORD,B.L.Jr., J.Chem.Phys. 6, 223 (1938).

136. WILSON,E.B.Jr., DECIUS,J.C. and CROSS,P.C., Molecular Vibrations, McGraw-Hill, New York 1955.

137. WU,T.Y., Vibrational Spectra and Structure of Polyatomic Molecules, Edwards, Ann Arbor, Mich. 1946.

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